of lead nitrate irradiated with 50 Mrad of ^{60}Co γ-rays with the substance irradiated close to the reactor core so as to receive the above dose of γ-rays and, in addition, 5×10^{15} nvt fast and $2 \cdot 2 \times 10^{16}$ nvt slow neutrons. In the latter case,

FRACTION ANNEALED, φ

150 °C
O LEAD NITRATE, γ
Δ LEAD NITRATE, $\gamma + n$
$\square$ LEAD NITRATE $(10^{-2} Al), \gamma$
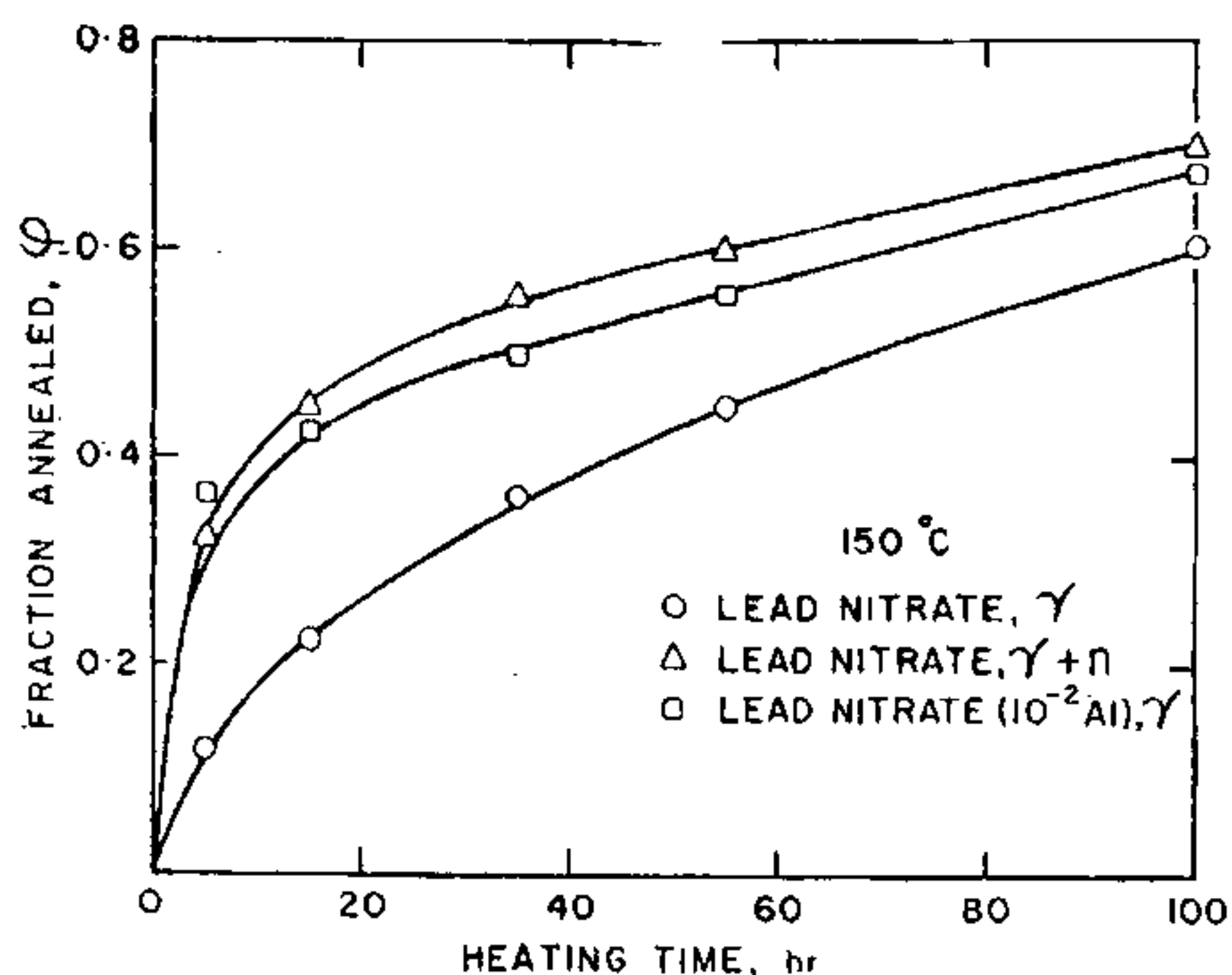
HEATING TIME, hr
FIG. 1.

apart from the chemical damage produced by the γ-rays, and the 45 Kev ^{14}C atoms and the $0 \cdot 56$ Mev protons from the $^{14}N(n, p)^{14}C$ reaction, a considerable concentration of displacements is produced by the knock-on collisions of chiefly the fast neutrons. The initial chemical damage in irradiation with only γ-rays (1670 ppm) is smaller than that with γ-rays *plus* neutrons

(2922 ppm). The annealing rate is higher in the latter case (Fig. 1). For example, the fraction annealed on 35 hr. heating at 150° C. was $0 \cdot 366$ for the γ-irradiated lead nitrate and $0 \cdot 560$ for the substance irradiated in the reactor. It has been already found[5] that the annealing characteristic at a given temperature is independent, over wide limits, of the energy, the dose rate and the dose of γ-rays. It would appear therefore that lattice defects are responsible for the higher annealing observed with the reactor irradiated lead nitrate than with the substance irradiated with only γ-rays.

1. Andersen, T. and Maddock, A. G., *Trans. Faraday Soc.*, 1963, **59**, 2362, and references therein.
2. Mohanty, S. R. and Upadhyay, S. R., *Ind. J. Chem.*, 1963, **1**, 456
3. — and —, *Nature*, 1963, **199**, 169.
4. — and —, *Ibid.*, 1964, **201**, 921.
5. Andersen, T. *Ibid.*, 1963, **200**, 1094.
6. Khare, M. and Mohanty, S. R. (To be published).
7. Pick, H. and Weber, H., *Z. Physik*, 1950, **128**, 409.
8. Mohanty, S. R., *Ph.D. Thesis*, Cambridge University, 1960.

OXIDATION OF THIOUREA BY AMMONIUM HEXANITRATO CERATE IN TRI-*n*-BUTYL PHOSPHATE

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A SOLUTION of ammonium hexanitrato cerate in tri-*n*-butyl phosphate suitably diluted with carbon tetrachloride (1 : 4 by volume) has been observed to be a good oxidising agent for the potentiometric titrations of hydroquinone, sodium iodide, ascorbic acid, ferrous chloride and potassium ferrocyanide dissolved in either glacial acetic acid or TBP-carbon tetrachloride mixed solvent.[1] The same reagent taken in excess has been found to oxidise thiourea dissolved in glacial acetic acid quantitatively to formamidine disulphide base. One equivalent of the oxidising agent is consumed for every mole of thiourea. An analytical procedure has been evolved for the estimation of thiourea dissolved in acetic acid, based on this reaction.

$0 \cdot 02$ M solution of ammonium hexanitrato cerate in the TBP-carbon tetrachloride mixed solvent is prepared from the stock solution. The exact strength of such a solution is determined before use by titrating with a standard solution of ferrous ammonium sulphate employing ferroin as an indicator. The strength of the oxidising agent is also checked by titrating potentiometrically with a standard solution of hydroquinone.[1]

$0 \cdot 025$ M solution of thiourea is prepared by dissolving $0 \cdot 09515$ g. of recrystallized thiourea in 50 ml. of glacial acetic acid.

$0 \cdot 025$ M solution of hydroquinone is prepared by dissolving $0 \cdot 1376$ g. hydroquinone in 50 ml. glacial acetic acid or TBP-carbon tetrachloride mixed solvent.
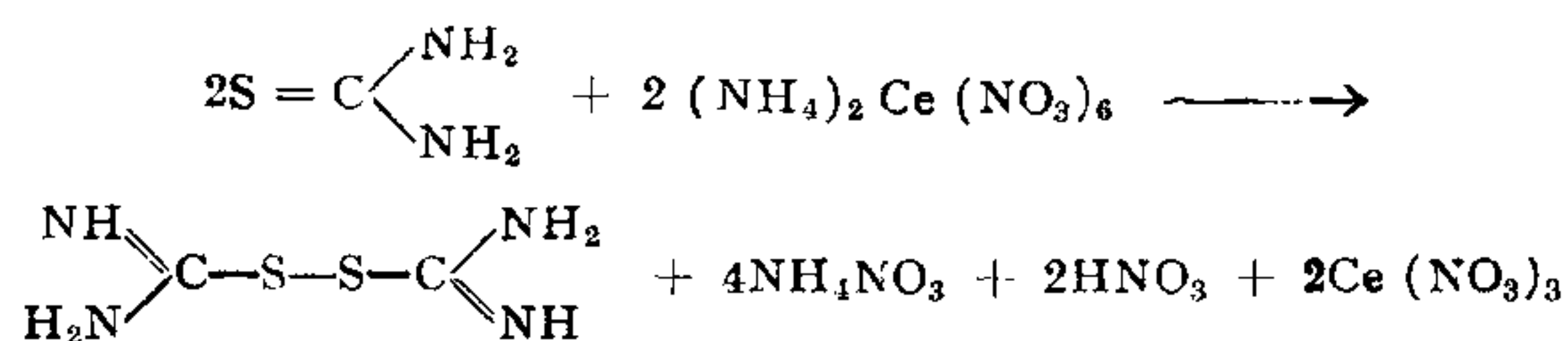
3

An aliquot of thiourea solution (10–70×10^{-6} moles) is added to an excess of cerate (60–200×10^{-6} moles) taken in the potentiometric cell and diluted with glacial acetic acid to about 20 ml. The excess cerate is titrated back potentiometrically with hydroquinone, employing glass electrode-platinum electrode couple. A sharp fall in potential is noticed at the end point of the titration. The titre values are quite reproducible. The analytical results of a few representative experiments are given in Table I.

TABLE I

Oxidation of thiourea by ammonium hexanitrato cerate in tri-n-butyl phosphate

Sl. No.	Amount of thiourea taken moles $\times 10^6$	Total amount of cerate taken moles $\times 10^6$	Amount of cerate present in excess moles $\times 10^6$	Amount of cerate consumed moles $\times 10^6$	Per cent. error
1	16·75	87·00	70·25	16·75	0
2	61·43	121·80	60·70	61·10	−0·05
3	71·59	205·24	134·06	71·18	−0·05
4	22·34	69·60	47·05	22·55	+0·09

It is clear from the titre values given in the table that one mole of thiourea consumes one equivalent of the oxidant. The probable product of oxidation could be formamidine disulphide and the reaction may be represented as follows :

$$2S = C{\Large\langle}{}^{NH_2}_{NH_2} + 2\,(NH_4)_2\,Ce\,(NO_3)_6 \longrightarrow$$

$$\underset{H_2N}{\overset{NH}{\Large\rangle}}C\!-\!S\!-\!S\!-\!C{\Large\langle}{}^{NH_2}_{NH} + 4NH_4NO_3 + 2HNO_3 + 2Ce\,(NO_3)_3$$

Similar observations have been made with other oxidising agents also. For instance, an aqueous solution of iodine oxidises thiourea to formamidine disulphide in acid medium and one equivalent of the oxidant is consumed per mole of thiourea reacted.[2] On the other hand, in alkaline medium the sulphur atom present in the thiourea molecule is converted into sulphuric acid and urea is the other product of oxidation by iodine.[3] Other oxidising agents such as potassium permanganate, hydrogen peroxide, potassium chlorate, sodium nitrite, ferric chloride and copper (II) salts are observed to oxidise thiourea to different oxidation products depending on the experimental conditions.[4-9]

Although a solution of ammonium hexanitrato cerate in acetonitrile oxidises thiourea it is found that the reaction does not exactly correspond to the formation of formamidine, as the oxidant consumed is always greater than one equivalent.[10] It is, therefore, not possible to make use of such a solution for the estimation of thiourea in non-aqueous solution. However, ammonium hexanitrato cerate in tri-n-butyl phosphate offers more accurate results and therefore it could be employed for the estimation of thiourea in non-aqueous media.

1. Mruthyunjaya, H. C. and Murthy, A. R. V., *Ind. J. Chem.*, 1967, **5** (8).

2. Reynolds, J. E. and Werner, E. A., *J. Chem. Soc.*, 1903, **83**, 1.

3. Skvamovsky, S., *Chem. Zentr.*, 1941, **2**, 379 (*cf.* Kolthoff, I.M., *Volumetric Analysis*, III. Interscience Publishers, Inc., New York, 1957, **3**, 387).

4. Werner, E. A., *J. Chem. Soc.*, 1919, **115**, 1168.

5. —, *Ibid.*, 1912, **101**, 2166.

6. Khodaskar, S. N., Bhobe, R. A. and Khanolkar, D. D., *Sci. and Cult.*, 1967, **33**, 191.

7. Kratochvil, B., Zatko, D. A. and Markuszewski, R. *Anal. Chem.*, 1966, **38**, 770.

8. Mruthyunjaya, H. C. and Murthy, A. R. V. (Communicated to *Z. Anal. Chem.*).

9. — and — (Communicated to Talanta).

10. Rao, G. P., *Ph.D. Thesis*, Indian Institute of Science, Bangalore, 1964.