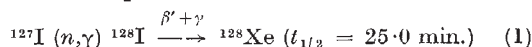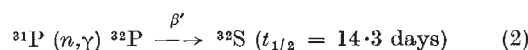## Radioactivation Analysis of Phosphorus in Iodine

AN important method in the preparation of pure silicon for semiconductor devices is the silicon iodide process[1]. In this method silicon tetraiodide is formed from the elements and purified by fractional distillation before being decomposed by passage over a heated tantalum filament. We have found by radioactivation analysis[2] that the predominating N-type impurity in silicon produced by this method in our laboratory is phosphorus, and that its concentration seems to be largely independent of the phosphorus content of the 'crude' silicon. This could be explained if there was an appreciable phosphorus-level in the iodine used, as the mass ratio of silicon to iodine in the above reaction is about one to twenty. Therefore we developed the following method for estimating the phosphorus content of iodine.

On irradiating iodine which contains phosphorus in a thermal neutron flux, the following nuclear reactions take place.

$$^{127}I\ (n,\gamma)\ ^{128}I \xrightarrow{\beta'+\gamma}\ ^{128}Xe\ (t_{1/2} = 25\cdot0\ \text{min.}) \quad (1)$$

and

$$^{31}P\ (n,\gamma)\ ^{32}P \xrightarrow{\beta'}\ ^{32}S\ (t_{1/2} = 14\cdot3\ \text{days}) \quad (2)$$

The half-life values show that if we allow sufficient time for the iodine activity to die away, the activity in the specimen will be entirely due to phosphorus and other long-lived impurities present. This is of considerable advantage in the handling of the activated samples, as no radiation shielding is required.

The reaction used for determining the phosphorus content is the following:

$$2P + 5I_2 + 8H_2O = 10HI + 2H_3PO_4 \quad (3)$$
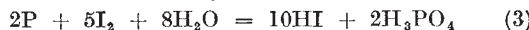
It is of paramount importance that the carrier added to the irradiated sample be in the same chemical form as the active element which is to be determined. This is achieved in the above reaction, as the phosphorus, whether present originally as the element or the iodide, ends up as an orthophosphate ion. The method also has the rather novel feature that the inactive phosphorus takes part in the reaction and, after conversion to phosphate, also acts as a carrier.

The details of the method are as follows. About $0\cdot5$ gm. samples of iodine were sealed in silica ampoules and irradiated for a week in the pile at Harwell together with 30 mgm. of diammonium hydrogen phosphate to act as a standard. On return, the ampoules were allowed to stand for a day to let the activity due to the iodine decay and were then cracked open and crushed in a percussion mortar. The mixture was transferred with great care into about 20 ml. of distilled water containing a suspension of 55 mgm. of red phosphorus (a weight in excess of the amount required for the reaction). As the reaction proceeded, iodine was dissolved in the hydriodic acid solution, giving an intense colour. The solution was warmed on a water bath until the iodine coloration had completely disappeared. The residual red phosphorus was then dissolved by adding excess inactive iodine, and standing the solution on the water-bath overnight. The fragments of the silica ampoule were then removed by filtration and the filtrate treated with hydrogen peroxide. Iodine crystals slowly appeared as the iodide complex was broken down and the iodine solubility consequently decreased. These crystals were filtered off. Chloro-

form was then shaken with the filtrate in a separating funnel to remove final traces of iodine. The procedure was repeated until the final aqueous solution was colourless.

The phosphate was then determined as the magnesium pyrophosphate in the same manner as we have previously reported[2]. Three methods were used for establishing the identity of the activity thus isolated. Absorption and decay measurements were made showing it to be a pure β-radiation with a half-life of fourteen days, and in some cases the solution and precipitation stages were again repeated, the results showing no loss in activity per gram. These facts indicate that, using the above technique, the phosphate isolated is radiochemically pure. The overall efficiency of the method is 70–80 per cent.

If one assumes that the maximum efficiency of the counting system is 25 per cent and that its detection limit is 20 counts per min. above background, then it can be shown that, for irradiation for a week at a pile factor of 10, the limit of the method is about $0\cdot003$ part per million on a gram sample. Phosphorus concentrations, which we have measured in iodine from various sources, have been found to vary between 10 and $0\cdot1$ parts per million. A sample of 'Analar' grade iodine was found to contain $0\cdot18$ p.p.m. of phosphorus.

We are indebted to colleagues in this laboratory for encouragement and assistance.

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Rugby. Dec. 22.

[1] Anderson, H. C., and Belz, L. H., J. Amer. Chem. Soc., 75, 4828 (1953).
[2] James, J. A., and Richards, D. H., Nature, 176, 1026 (1955).

Crystal Structure of p-Chlorbenzene Iododichloride

THE unexpected bond distances observed by Archer and van Schalkwyk[1] in benzene iododichloride have indicated a class of organic compounds about which few structural data are at present available. We have therefore sought to confirm their findings by the examination of a related compound, p-chlorbenzene iododichloride.

Light-yellow needles of this compound are obtained by passing dry chlorine into a dry chloroform solution of p-iodochlorbenzene. Like other iododichloride compounds with an electrophilic group in the para position, giving rise to a dipole moment directed away from the iodine atom, p-chlorbenzene iododichloride appears to be moderately stable and certainly more so than unsubstituted benzene iododichloride (Table 1). It seems possible that the tendency of electrons to drift away from the iodine atom partially increases the positive charge on the iodine and so makes possible a greater resonance stabilization of the molecule[4].

Single-crystal X-ray oscillation and Weissenberg photographs, taken with copper and molybdenum K_α radiations, indicate a triclinic unit cell : $a = 10\cdot1_0$; $b = 4\cdot13$; $c = 11\cdot0_3 \pm 0\cdot04$ A. ; $\alpha = 96°\ 42'$; $\beta = 107°\ 27'$; $\gamma = 91°\ 12' \pm 36'$; where b is the needle axis. With the observed density, $2\cdot31$ gm./c.c., this corresponds to two molecules per unit cell. The centrosymmetric test[5] was used for deciding between the two alternative space groups. This shows clearly that the $(h0l)$ projection must be centrosymmetric,