# NOTES.

## *The Rapid Determination of Copper in its Alloys.* By PHILLIP M. FISK, ALEX. LIBERMAN, and FRANCIS F. POLLAK.

THE two usual methods for the routine analysis of copper alloys suffer from various disadvantages, the electrolytic method from the time required, and the iodometric method from the number of operations necessary to obtain a nitrite-free solution of the correct $p_H$ range. We have derived the following method, which can be carried out in 12 mins., including the drilling of samples.

Alloy corresponding to 0·20—0·25 g. of copper is dissolved in 10 ml. of 5N-nitric acid, and the solution warmed until nitrous fumes have disappeared, and then immediately cooled. 10 Ml. of a solution containing 100 g. of urea and 300 g. of ammonium acetate per l. are added, and the sides of the conical beaker are washed down by 25 ml. of water. 2 G. of potassium iodide are then added, and after 1 min., the liberated iodine is titrated with sodium thiosulphate solution containing 39 g. per l. (1 ml. = 0·01 g. of copper, standardised against pure copper).

Lead-containing alloys give a coffee-coloured suspension at the end-point, owing to the presence of lead iodide. We have failed to overcome this disadvantage either by keeping the lead in solution or by converting it into white precipitates, but experiments with ammonium chloride appear promising.

Iron does not usually occur in such alloys in sufficient quantity to affect the accuracy, but its interference can be suppressed by addition of sodium phosphate, as usual.

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### *The Melting Points of Toxicarol and of Related Compounds.* By STANLEY H. HARPER.

THE author (J., 1940, 1178) directed attention to the discrepancies between the published m. p.'s for *dl*-α-toxicarol which could not be accounted for by the presence of *dl*-β-toxicarol. Recently, however, Jones and Wood (*J. Amer. Chem. Soc.*, 1941, **63**, 1760) have shown that the type of glass from which the capillary tubes are made has a marked effect on the m. p. of *dl*-α-toxicarol, a higher value being observed in hard- than in soft-glass tubes. The m. p. of the pure *dl*-α-toxicarol described previously (Harper, *loc. cit.*) has therefore been redetermined, and observations extended to other members of the rotenone group. M. p.'s were determined in Mason's electrically heated apparatus (*Chem. and Ind.*, 1925, 577), short-range Anschütz thermometers being used. The substance was inserted in the block at 5—10° below the m. p. and heated at a rate of 1° per minute. Temperatures are uncorrected, but the calculated correction at the highest temperature was only 1°.

| | M. p. in soft glass. | M. p. in Pyrex glass. | | M. p. in soft glass. | M. p. in Pyrex glass. |
|---|---|---|---|---|---|
| *dl*-α-Toxicarol | 219—223° | 231—232° | *dl*-Deguelin | 164—165° | 170—171° |
| *l*-α-Toxicarol | 125—127 | 125—127 | Rotenone | 163·5—164·5 | 167—168 |
| *l*-α-Dihydrotoxicarol | 178—179 | 185·5—186·5 | *l*-*iso*Rotenone | 179—180·5 | 184·5—185·5 |
| *dl*-β-Toxicarol | 169—170 [1] | 169—170 [1] | *dl*-*iso*Rotenone | 171·5—172·5 | 172—173 |
| Sumatrol | 188—189 | 199—200 | *l*-Elliptone | 171—172 [3] | 178·5—179·5 [4] |
| *l*-Malaccol | 249—250 [2] | 249—250 [2] | *dl*-Elliptone | 176—177 | 180—181 |

[1] The melt was quite clear at the higher temperatures. [2] Partial melting and resolidification occurred at 225—227° (cf. J., 1940, 309). [3] A few crystals melted at 159—160° but the remainder not until the higher temperature. [4] A few crystals melted at 162° but the remainder not until the higher temperature.

The new m. p. for *dl*-α-toxicarol is now in close agreement with that recorded by Jones and Wood (*loc. cit.*) and by Cahn, Phipers, and Boam (J., 1938, 513). It is evident that if the effect is due to the alkalinity of the glass it only becomes apparent at temperatures above 130°, for the melting point of *l*-α-toxicarol is not affected by the type of glass used. It is noteworthy that all fusions of *l*-α-toxicarol reported previously (Harper, *loc. cit.*) were carried out in hard-glass or silica tubes and no racemisation was observed. No significant difference was observed with *dl*-β-toxicarol, although Jones and Wood record a slight raising in Pyrex glass, but this may well have been due to contamination with *dl*-α-toxicarol, for their specimens did not melt sharply. A marked raising of m. p. was observed with sumatrol, suggesting that the divergencies recorded previously [189° and 192°, Cahn and Boam (*J. Soc. Chem. Ind.*, 1935, **54**, 42T); 192—194° and 195—196°, Robertson and Rusby (J., 1937, 497)] may have been due in part to the type of glass used.

The m. p. of *l*-elliptone is higher than that recorded previously (Harper, J., 1939, 1099), and the proximity of this to that of *dl*-elliptone suggested racemisation at or near the m. p., a phenomenon already observed with malaccol (Harper, J., 1940, 309). However, after fusion at 180° for 15 minutes in a Pyrex tube, the specific rotation of *l*-elliptone was unchanged ($[\alpha]_D^{20^\circ}$ +55° in acetone). Racemisation does not therefore occur under these conditions, and the differing m. p.'s must be due to dimorphism, a feature common in this group of compounds.—DEPARTMENT OF INSECTICIDES AND FUNGICIDES, ROTHAMSTED EXPERIMENTAL STATION, HARPENDEN, HERTS. [*Received, November* 5*th*, 1941.]