Toxicological and Forensic

Toxicological Detection of Thallium. H. Kluge. (*Z. Unters. Lebensm.*, 1938, **76**, 156–159.)—A new method for the detection and determination of thallium in toxicological material depends upon its conversion into thallic chloride ($TlCl_3$ or $TlHCl_4$), which can be extracted from aqueous solution with ether (Shaw, *Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 93; Abst., ANALYST, 1933, **58**, 358). Thallous iodide is precipitated from the extract and determined gravimetrically or colorimetrically. A portion of the material not exceeding 70 g. is decomposed by treatment with hydrochloric acid and potassium chlorate, and, when decomposition is complete, the liquid is washed through a glass-wool filter with hot water and the filtrate is made up to 100 ml. or 250 ml. and filtered. An aliquot portion (90 per cent.) of the filtrate is shaken with ether until a colourless extract is obtained. The aqueous liquid is treated with chlorine and re-extracted with ether. The residue left after evaporation of the combined ethereal extracts is treated with nitric acid

and hydrogen peroxide until organic matter is destroyed, evaporated almost to dryness, and dissolved in water, and the solution is concentrated on the water-bath to a small volume (0·5 ml. for small amounts of thallium). The solution is then made slightly alkaline with 25 per cent. ammonia solution and heated with excess of 20 per cent. potassium iodide solution. The precipitate of thallous iodide is allowed to stand overnight and collected in a Gooch crucible, the filtrate being used to transfer the last portion. The precipitate is washed once with water and then with alcohol, and dried at 100° C. and weighed (Factor TlI to Tl = 0·6169). For an amount of thallium of the order of 1 mg. colorimetric determination is preferable. The precipitation of thallous iodide is carried out in a centrifuge tube, in which it is washed by centrifuging with alcohol until free from potassium iodide. It is then treated with 1 or 2 drops of conc. sulphuric acid and, when decomposition is complete, with 1 ml. of water, 1 to 3 drops of 10 per cent. sodium nitrite solution and 0·5 ml. of chloroform. After vigorous shaking, the chloroform layer is allowed to separate and is compared colorimetrically with equal volumes of chloroform containing known amounts of iodine. A series of standards may be prepared by precipitation of thallous iodide from a solution of thallium sulphate containing 1 mg. of thallium per ml. or a solution of potassium iodide (0·8123 g. per litre; 1 ml. = 1 mg. Tl) may be treated with sulphuric acid, sodium nitrite and chloroform. The ratio of 1 ml. of aqueous liquid to 0·5 ml. of chloroform should be maintained in all comparison tubes. The limit of the colorimetric method is 0·05 mg. of thallium. The precipitated thallous iodide may be examined spectroscopically. Control experiments indicated that the method has an accuracy of 99 per cent. The distribution of thallium in the organs of a young dog (weighing 3·77 kg.) poisoned with 1 g. of thallium sulphate (= 0·81 g. of thallium) was investigated. Of the amount administered about 15 hours before death, 38·52 per cent. was located. The percentage distribution of this amount was as follows:—stomach, 75·88; intestines, 14·25; liver, 5·32; lungs, 2·49; kidneys, 1·62; spleen, 0·27; heart and heart-blood, 0·18. A. O. J.

Lead Content of Human Blood. C. E. Willoughby and E. S. Wilkins, Jr. (*J. Biol. Chem.*, 1938, **124**, 639–657.)—The method used for finding the lead content of the blood was the dithizone method described by the authors previously (*Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 33, 285) with the following modifications. After complete solution of the digestion residue by the chloride and hydrochloric acid reagent, ammonium hydroxide (sp.gr. 0·90) is added rapidly until precipitation of the ferric hydroxide is complete, after which the excess is boiled off and the precipitate is immediately dissolved by the addition of 5 ml. of 4 per cent. citric acid solution to the mixture. The liquid is then partly neutralised by adding about 6 drops of ammonium hydroxide before the addition of the potassium cyanide. Later, and only when blood specimens are being examined, the lead dithizone complex, resulting from the initial lead separation, is not washed with dilute potassium cyanide before conversion into lead nitrate. It is shaken with 20 ml. of 1 per cent. nitric acid instead of being extracted twice with 10-ml. portions of acid. The optimum *p*H for the final extraction of the lead nitrate solution has been found to be 7·5 to 8·3.

Analyses were made of blood specimens from 189 individuals, in none of whom was any prior undue exposure to lead reported, and none of whom showed any signs or symptoms of lead poisoning; the proportion of lead found varied from 0·0 to 0·09 mg. per 100 g. of blood, with a most probable value of 0·025 ± 0·012 mg. of lead, which is significantly lower than found by most previous investigators. This may be accounted for by the methods and techniques used by the various workers, by geographical location or possibly, but not probably, by the fact that the individuals now tested were not in normal health when samples were taken. Of the 189 specimens analysed, 58 were separated into serum and cells and fibrin for individual analyses of these fractions, and approximately 90 per cent. of the serum samples contained no detectable amount of lead. It is concluded that 0·09, and even 0·10 mg., of lead may occasionally occur without indisputable clinical evidences of plumbism being present. D. G. H.

Acetone Chlorohaemin in Blood Testing. A. F. Richter and M. Hofman. (*Z. anal. Chem.*, 1938, **113**, 334–339.)—In Wagenaar's adaptation (ANALYST, 1936, **61**, 268) of Nencki and Zaleski's reaction (*Z. physiol. Chem.*, 1900, **30**, 384) for blood, which is based on the formation of crystals of "acetone-haemin," the addition of a mineral acid, and in particular of hydrochloric acid, is specified. It is now pointed out that the substance formed is acetone chlorohaemin, $C_{34}H_{32}N_4O_4FeCl.CH_3COCH_3$, and that the reaction can be produced by crystallisation of an extract in acetone and oxalic acid of the blood coagulum (*cf.* Hamsík, *id.*, 1930, **190**, 199) without addition of a mineral acid. Since the use of perchloric acid produces crystals, which according to analyses and qualitative tests contain no ClO_4-radical, it is believed that the nature of the acid added is irrelevant so long as Cl′-ions are present in the blood. It was not possible to produce an analogous iodine compound. Mineral acid aids the transformation from the α- to the β-structure (the Teichmann transformation) on heating, but the authors disagree with Wagenaar's conclusion (*Z. anal. Chem.*, 1930, **79**, 110) that this occurs when the acetone chlorohaemin is heated at 105° C. for 2 hours. They removed lipoids from this substance by extraction with petroleum spirit, and raised its temperature from 28° to 192° C. in 6 hours, and then maintained it at 192° C. for 1 hour. The Hamsík reagent for α-structure (*Pub. Fac. Med. Univ. Masaryk*, 1923, **2**, 1), *i.e.* a 5 per cent. solution of potassium hydroxide in methyl alcohol, then gave a positive result, and this reaction is suggested as preferable to the Teichmann reaction as a test for blood. The resulting crystals (which are illustrated) form characteristic star-shaped groups of needles, and after recrystallisation appear as opaque rosette-shaped clusters. Addition of imidazole produces ruby-red crystals of an addition compound (Hamsík, *Z. physiol. Chem.*, 1936, **241**, 156). On the other hand, the Wagenaar–Teichmann reaction gives crystals of chlorohaemin, which have the β-structure and are less characteristic, being opaque acorn-shaped groups consisting largely of 6-sided crystals with irregular outlines. In further experiments the acetone chlorohaemin was heated in 30 minutes to 250° and 280° C. (*cf.* Wagenaar, *loc. cit.*). When the temperature was maintained at 250° C. for 40 minutes, the Hamsík reaction was negative, and Wagenaar's test gave a doubtful result. It is concluded that the temperature of

250° C., suggested by Wagenaar, is too high, and that 240° C. is the maximum temperature for the Hamsík reaction. The haemochromogen reaction cannot be used as an indication of structure, since it is also given by β-haemin. J. G.