NOTES.

A Rapid Volumetric Method for the Determination of Lead in Brass. By PHILLIP M. FISK and FRANCIS F. POLLAK.

THE estimation of lead in brass, except for traces, is normally based on its separation by electrolysis or by precipitation as sulphate. Electrolysis, is rendered difficult in the presence of interfering elements, and the sulphate method needs a tedious separation from the matter insoluble in nitric acid. Starting from the impure sulphate, a number of methods have been developed, such as the molybdate and the chromate method, having in common the use of ammonium acetate as a solvent for lead sulphate before the final determination. Direct precipitation as chromate without preliminary separation as the sulphate under conditions described below is, however, more rapid and accurate.

Special Solutions Required.—Nitric acid, 1 : 1 by vol. Potassium dichromate, saturated. Phosphoric–sulphuric acid mixture : 100 ml. of phosphoric acid (*d* 1·75) and 180 ml. of sulphuric acid (*d* 1·8) made up to 1 l. Ferrous ammonium sulphate : 20 g. in 50 ml. of 20% sulphuric acid made up to 1 l. Sodium diphenylaminesulphonate indicator : 0·5 g. of sodium sulphate in 10 ml. of water added to 0·32 g. of the barium salt in 90 ml. of water and filtered.

Method.—For 1—4% of lead, 1·5 g. of drillings are dissolved in 15 ml. of the nitric acid in a 400-ml. conical beaker. The solution is heated to expel nitrous fumes, diluted to 100 ml., cooled, and neutralised with anhydrous sodium carbonate. Glacial acetic acid is added to dissolve the precipitate and then 10 ml. in excess. It may be found more convenient to use ammonia instead of sodium carbonate, but as an excess of ammonium acetate has a distinct solvent action on lead chromate, ammonia should be added until the precipitate first formed just dissolves : about 30 ml. of 5N-ammonia, followed by 15 ml. of glacial acetic acid, is convenient. To the acetic acid solution, 10 ml. of saturated potassium dichromate diluted to 20 ml. are added. After 3 mins.' boiling, the lead chromate becomes orange and dense ; on settling, it is filtered off through an 11-cm. No. 41 Whatman filter paper. Beaker and filter are washed free from soluble chromate with hot 5% acetic acid and finally with hot water. The filter-paper containing the precipitate is placed into the original beaker, and 25 ml. of the acid mixture washed down the sides of the beaker. The lead sulphate produced is dissolved on shaking by the addition of 5 g. of solid ammonium chloride. The solution is made up to 120 ml. with cold water. Fragments of filter-paper do not interfere with the subsequent titration. 25 Ml. of ferrous ammonium sulphate solution are added from a pipette, excess being titrated with N/20-potassium dichromate, 3 drops of sodium diphenylaminesulphonate solution being used as indicator, to a purple colour which persists on shaking. The ferrous ammonium sulphate is standardised by using 25 ml. of the solution, 25 ml. of acid mixture, 100 ml. of water, and 3 drops of indicator. The difference in the volumes of dichromate in ml. $\times 0{\cdot}003453 =$ weight of lead in g. The dichromate solution is standardised against pure lead, taken through all the foregoing steps. The time for the lead estimation is 30 mins.

Interfering Elements.—Copper, cadmium, zinc, manganese, iron (III), aluminium, nickel, and cobalt do not interfere. Tin, converted into metastannic acid, will occlude alkali chromate, but up to 0·015 g. (*i.e.*, 1% Sn) this is negligible. Therefore, up to 1% of tin it is not necessary to filter off the metastannic acid before precipitation of the chromate. Antimony would give similar results, but it is almost absent in normal brasses and can be ignored. Arsenic yields lead arsenate insoluble in acetic acid, but does not interfere up to 0·0015 g. (*i.e.*, 0·1% As), as lead chromate is produced with excess of the dichromate. Bismuth may be ignored up to 0·1% if an excess of 15 ml. of acetic acid is used. Addition of citric acid before filtration offered no advantage. Phosphorus gives lead phosphate, insoluble in acetic acid, but up to 0·015 g. (*i.e.*, 1% P) the excess of dichromate converts the phosphate into the chromate and in any case most of the phosphorus present will be precipitated with the tin during solution in nitric acid.

A solution of nitrates of the following metals, giving impurities at least 10 times those normally present in commercial brass, gave results far more accurate than those obtained by the sulphate method: Cu, 55·50; Zn, 34·81; Pb, 2·77; Cd, 0·93; Ni, 1·73; Co, 0·84; Mn, 1·71; Fe, 0·86; Al, 0·85% (Found: Pb, by chromate method, 0·0485, 0·0487, 0·0487 g.; by sulphate method, 0·0479, 0·0478, 0·0480 g. Taken: Pb, 0·0486 g.).

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Some Notes on the Condensation Products of Acetaldehyde. By Ernest E. Connolly.

Aldol.—It is well known that the condensation of acetaldehyde under the action of alkaline catalysts yields aldol. This is usually described (*e.g.*, Heilbron, " Dictionary of Organic Chemistry ") as a viscous liquid, d^{15° 1·11, but it is doubtful if this is true acetaldol. The normal product of the condensation of acetaldehyde at room temperature, with a catalyst such as sodium hydroxide, is a colourless, somewhat syrupy liquid, d^{20° *ca.* 1·06. This " crude aldol " contains some 35% by weight of recoverable acetaldehyde. Further condensation, with increase of density to about 1·11, may be effected by stirring the crude aldol with 0·5% of calcium hydroxide; the product is miscible with water, but on distillation with dilute mineral acid it yields no more crotonaldehyde than the original crude aldol, but only enhanced quantities of higher-boiling unsaturated aldehydes, amongst which have been identified two hexadienals and one octatrienal. On reduction, these yield primary higher alcohols found in the crude butanol from the hydrogenation of technical crotonaldehyde. The aldol condensation products studied by Plant (J., 1938, 536) are probably of this nature.

Of the recoverable aldehyde present in crude aldol, only about one-half is readily removed at room temperature by a current of inert gas or application of vacuum. The remaining half appears to be set free very slowly and is possibly present as the " semiacetal " postulated by Shilov (*J. Appl. Chem. U.S.S.R.*, 1935, **8**, 93). Substantially the whole of the unreacted aldehyde may, however, be removed by distillation with benzene or by passing the neutralised crude aldol through a tube at 100°. The residual product in both cases, however, crystallises as paraldol.

By the vacuum fractionation of crude aldol or paraldol there is obtained a colourless mobile liquid, b. p. 75°/16 mm., d^{20° 1·01. This quickly starts to polymerise, with evolution of heat, giving " viscid aldol " and finally crystalline paraldol. The change is accelerated by traces of electrolytes and this presumably unimolecular aldol cannot be stabilised by addition of pyridine, quinol, or resorcinol. It appears, however, to be fairly stable at −80°.

The rapid polymerisation of the mobile aldol makes it difficult to determine its properties, but by working as quickly as possible, the following results were obtained: d^{20° 1·009, n_D 1·4280, whence $[R_L]_D$ 22·44, indicating coupling through one oxygen atom; *M* (cryoscopic in benzene), 88, 89. Viscid and mobile aldol have been mentioned by Nowak (*Monatsh.*, 1901, **22**, 1140); the former is probably chiefly supercooled paraldol.

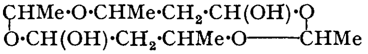
Paraldol.—The molecular weight of crystalline paraldol (cryoscopic in benzene) was found to be 175, 175. In the supercooled liquid state it showed d^{20° 1·116, $n_D^{20^\circ}$ 1·4610, giving $[R_L]_D$ 43·26. If we take $[R_L]_D$ for aldehyde as 11·51, the fall in refraction in passing to paraldol is 4 × 0·69, indicating a coupling through all the oxygen atoms present. Paraldol is therefore probably cyclic, like paraldehyde, and it is possible also that there is an aldol–paraldol equilibrium.

By the hydroxylamine salt method paraldol is titrated quantitatively as aldol, and by fractionation from dilute acid it yields crotonaldehyde quantitatively.

Higher Condensation Products.—A condensation product not hitherto described is obtained by stirring crude aldol with 2% of sulphuric acid for some hours, followed by neutralisation, water washing, and vacuum fractionation. It is a colourless, viscid liquid, b. p. 136°/17 mm., nearly insoluble in water: d^{20° 1·063, $n_D^{20^\circ}$ 1·442; *M* (cryoscopic in benzene), 245, 247.

With aqueous or alcoholic hydroxylamine hydrochloride, there was only a small immediate reaction, probably due to a little aldol still present. After overnight standing, however, titration showed 1 c.c. of N-sodium hydroxide = 0·0629 g. of the substance. Distillation from dilute sulphuric acid, and collection in ice-water gave a similar total figure for the titration of the distillate: 1 c.c. of N-alkali = 0·0651 g. Analysis of the distillate and calculation back to *M* 246 showed that 1 mol. gave 1·95 mols. of acetaldehyde and 1·92 mols. of crotonaldehyde. The production of acetaldehyde and crotonaldehyde in equimolecular proportion was confirmed on a 100-g. sample by fractional distillation.

The substance shows no immediate reaction with aqueous bromine. It is suggested tentatively that it is a doubled form of Shilov's " cyclic semi-acetal," *i.e.*, as inset. With the vacuum-distillation facilities available, slight decomposition during distillation could not be avoided, so a high degree of purity could not be attained. The liquid also showed no signs of crystallising down to −80°.



$$\begin{array}{l}\mathrm{CHMe{\cdot}O{\cdot}CHMe{\cdot}CH_2{\cdot}CH(OH){\cdot}O}\\ \mathrm{O{\cdot}CH(OH){\cdot}CH_2{\cdot}CHMe{\cdot}O\text{——}CHMe}\end{array}$$

Higher-boiling substances of similar character are present in the viscous distillation residue. Similar, almost resinous, water-insoluble products are obtained by long storage of slightly acid crude aldol in a vacuum.

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