

lysed for 4 hr. with 30 ml. 10 per cent hydrochloric acid and evaporated *in vacuo* again. The residue was dissolved in 10 ml. water, decolorized, evaporated to half volume of the solution *in vacuo*, diluted with 5 ml. methanol, and adjusted to pH 7.0 with aqueous ammonia. After standing overnight, 1.5 gm. of phenylalanine was obtained; m.p. 261.5° C.  $[\alpha]_D^{15} = +9.25^\circ$  (c., 9 per cent in water). Analysis: calculated for  $C_9H_{11}O_2N$ : N, 8.48; found, N, 8.23. This compound had the same  $R_F$  value as the standard phenylalanine.

**Hydrogenation of 4-benzylidene-2-methylloxazol-5-one.** 5 gm. of 4-benzylidene-2-methylloxazol-5-one was hydrogenated with the same catalyst in 50 ml. methanol at 75° C., 90 kgm./cm.<sup>2</sup>. The reaction mixture was filtered, evaporated *in vacuo*, hydrolysed for 4 hr. with 30 ml. 10 per cent hydrochloric acid. The acid solution was extracted with ether, and the water layer was evaporated *in vacuo*. The residue was dissolved in 10 ml. water, decolorized, concentrated to 3 ml., diluted with 3 ml. methanol, adjusted to pH 7 with aqueous ammonia. After standing overnight, 0.7 gm. of phenylalanine was obtained; m.p. 280° C.  $[\alpha]_D^{20} = +12.5$  (c., 9 per cent in water). Analysis: calculated for  $C_9H_{11}O_2N$ : N, 8.48; found, N, 8.23. This compound was identified by paper chromatography.

**Hydrogenation of  $\alpha$ -benzildioxime.** 5 gm. of  $\alpha$ -benzildioxime was hydrogenated in 10 per cent ammoniacal methanol at 80° C., 80 kgm./cm.<sup>2</sup>, with the same catalyst, and the product was recrystallized from *n*-butanol. Diphenylethylenediamine (2.5 gm.) was obtained. Analysis: calculated for  $C_{14}H_{16}N_2$ : C, 79.21; H, 7.60; N, 13.20; found: C, 78.05; H, 7.20; N, 12.12.  $[\alpha]_D^{15} = +8.75$  (800 mgm./100 ml. of ether);  $[\alpha]_D^{15} = +431.0$  (29.6 mgm./100 ml. of ether). (In this experiment, we observed the wide variation of  $[\alpha]_D$  of diphenylethylenediamine with the concentration of the substance in diethyl-ether.)

It appeared that the palladium adsorbed on the supporter having the asymmetric configuration was capable of catalysing the asymmetric reduction.

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### A New Reagent for the Determination of Thorium

SEVERAL organic acids<sup>1-4</sup> have been used for the quantitative precipitation of thorium. By a careful control of the pH value, thorium may be separated from the rare earths. The precipitate in most cases is rather of indefinite composition, and for a quantitative determination, it has to be ignited to thorium oxide and weighed. We have been engaged in investigating derivatives of cinnamic acid to see if they possess any advantages over other acids which have been employed hitherto.

It was found that *m*-nitro cinnamic acid not only gives a clear-cut separation of thorium from other trivalent rare-earth ions, but also gives a thorium precipitate of definite composition. The precipitated thorium salt is the tetra-*m*-nitro cinnamate and is one of the very few examples of precipitation of thorium as the tetravalent salt.

An alcoholic solution of *m*-nitro cinnamic acid was added to a solution of thorium salt at pH 2.0 or less and this was carefully adjusted to 3.8-4. The higher pH value is specially necessary when sulphate ions are present. Thorium came down as a granular precipitate. The precipitate was filtered, washed with hot alcohol and weighed as thorium tetra-*m*-nitro cinnamate. It was then ignited and weighed as thorium oxide. The following are typical results.

Weight of thorium tetra- <i>m</i> -nitro cinnamate (gm.)	0.1135
Weight of ThO <sub>2</sub> (by calculation) (gm.)	0.02997
Weight of ThO <sub>2</sub> (by ignition) (gm.)	0.0299

Thorium may therefore be determined by a direct weighing of the precipitate instead of by igniting, as has been done hitherto.

The same experimental procedure may be followed for separation of thorium from trivalent rare earths; if, however, the proportion of the rare earths is preponderantly high, a double precipitation may be followed.

Tetravalent ions like titanium, zirconium, cerium (ic), etc., are also precipitated by this reagent and would thus interfere.

Further details will be published elsewhere.

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<sup>1</sup> Moeller, T., Schweitzer, G. K., and Starr, D. D., *Chem. Rev.*, **42**, 63 (1948).

<sup>2</sup> Raghava Rao, Bh. S., *et al.*, several papers, cf. *J. Ind. Chem. Soc., J.S.I.R., Anal. Chem. Acta*, etc. (1946-55). Banks, C. V., and Byrd, C. H., *Anal. Chem.*, **25**, 416 (1953).

<sup>3</sup> Osborn, G. H., *Analyst*, **73**, 381 (1948). See also, "B.D.H. Book of Organic Reagents", 119 (London, 1946).

<sup>4</sup> Datta, S. K., and Banerjee, G., *Anal. Chim. Acta*, **12**, 23, 38 (1955).

### Recording Differential Thermogravimetric Balances

IN recent years, interest has been revived in the application of the thermogravimetric technique for the characterization of inorganic and organic compounds, and for studies concerning their thermal decomposition process. Several types of automatic balances have been developed—some of them now being commercially available—to give recorded curves of the cumulative weight-loss, with time or temperature, of a sample decomposing thermally under controlled conditions. It is often necessary to prepare, from this record, a curve of the rate of weight-loss as a function of time or temperature, by the somewhat tedious and relatively inaccurate process of graphical differentiation.

In order to assist our investigations on the thermal decomposition process of coal and related compounds, two types of thermogravimetric balances were devised to give automatically precise and continuous records of the differential weight-loss, together with