Indikatoren wurde in ihren Einzelheiten studiert. Gute Ergebnisse mit Rhodanid erhält man, wenn man durch einfache Verdünnung den pH der Eisenlösung auf 3·0–3·2 einstellt. Zugabe eines Puffers oder einer verdünnten Lösung einer starken Base zur pH-Einstellung gibt stets zu niedrige Ergebnisse. Chromazurol S ist als Indikator vorzuziehen, da der Farbumschlag schärfer ist und Titrationen in ziemlich sauren Lösungen (pH 1·25) möglich sind. Bis 50 mg Eisen in 100 ml Probe lassen sich mit einer relativen Standardabweichung von nur 2‰ bestimmen.

Résumé—On a étudié en détail le dosage direct de l'ion ferrique au moyen de cyclohexanediamine tétracétate disodique en utilisant, comme indicateurs, l'ion thiocyanate et le Chrome Azurol S. On peut obtenir de bons résultats avec l'indicateur au thiocyanate si le pH de la solution ferrique est ajusté entre 3·0 et 3·2 par simple dilution. L'addition d'un tampon ou d'une solution diluée de base forte pour ajuster le pH dans la zone désirée conduit toujours à des résultats faibles. On préfère l'indicateur Chrome Azurol S, car le virage de couleur est beaucoup plus net, et les dosages sont possibles en solutions relativement acides (pH 1·25). On peut doser jusqu'à 50 milligrammes de fer dans un échantillon de 100 millilitres, avec un écart type relatif de deux pour mille seulement.

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The preparation of cerium–IV hydroxide from ammonium hexa-nitratocerate by employing kinetically controlled precipitation through urea hydrolysis

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THE recovery of pure cerium-IV chemicals from thorium-freed monazite cerium-thorium sands involves the isolation of the cerium from the remaining rare earths by conversion to ammonium nitratocerate $(NH_4)_2Ce(NO_3)_6$.[1] A practical cerium-IV reagent which can be converted to sulphatoceric acid, $H_2Ce(SO_4)_3$, in sulphuric acid solution, for use as a standardised titrant, has previously been described.[1] The procedure involves the precipitation of $Ce(OH)_4$ by addition of a saturated aqueous solution of pure ammonium nitratocerate to a large excess of aqueous ammonia, followed by filtration of insoluble $Ce(OH)_4$, and washing this with water to eliminate ammonium salts. By this process the hydroxide is soluble in hot dilute sulphuric acid. If this $Ce(OH)_4$ is air dried, it forms a horny solid which must be ground to pass a 100-mesh sieve. The procedure here described for producing $Ce(OH)_4$ by kinetically controlled precipitation, employing urea, offers a much more practical preparation of ceric hydroxide, and avoids the difficult drying and grinding operation previously required.

Procedure

Add 1 pound of pure ammonium nitratocerate to a solution containing 1 pound of urea and 10 ml of concentrated nitric acid in a volume of 600 ml, in a 2000-ml covered Pyrex beaker, at boiling temperature. The resulting solution is dark red in colour and crystal clear. Keep the solution boiling briskly, adding water to replace that lost as vapour.

The boiling temperature after 30 min is approximately 110° and the colour of the solution is beginning to decrease. At 40 min the colour is dark orange; foaming to the extent of 25 mm results from the evolution of carbon dioxide from the urea breakdown. At 45 min precipitation begins, the precipitate being orange in colour. At 60 min the precipitate is lemon yellow and the solution temperature is 112°. At 75 min the precipitate is still lemon yellow, and foam is still being produced. At 90 min the reaction is complete, the solution is colourless, and the precipitate is grey-white.

Allow the reaction mixture to cool, and transfer the solution and precipitate to two polyethylene wide-necked 250-ml bottles with screw caps. Place the bottles in a pair of centrifuge trunion cups, and separate the precipitate from the parent solution by 5 min rotation at 1500 rpm and 250 mm displacement from the centre of rotation. (Trunion cups #844 of a No. 2 International Instrument Company centrifuge may be employed.) Pour off supernatant solution (pH approximately 12), add 150 ml of water to each bottle, stir well and repeat this centrifugal separation 5 or 6 times until the washings no longer give an ammonia test.

Transfer the $Ce(OH)_4$ thus prepared to a sheet of polyethylene and spread it out in a thin layer. The product air-dries in a few hours to give a finely divided pulverulent product. The yield is theoretical (approximately 37·95% of the weight of hexanitratocerate taken as raw material).

The finished product is readily soluble in hot dilute sulphuric acid to give a crystal clear solution that is stable on storage, and that may be heated to boiling without decomposition. It is not soluble in cold concentrated nitric or perchloric acid except after extremely long periods of storage.

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Summary—The preparation of cerium-IV hydroxide by kinetically controlled precipitation through use of the hydrolysis of urea and its reaction with ammonium hexanitratocerate is described. The air-dried product thus obtained is of fine-mesh particle size and is readily soluble in hot dilute sulphuric acid to form solutions of sulphatoceric acid, $H_2Ce(SO_4)_3$, for oxidimetric titrations.

Zusammenfassung—Die Darstellung von Cerhydroxyd durch kinetisch kontrollierte Fällung mittels Dissoziation von Harnstoff und Reaktion mit Ammoniumnitratocerat wird beschrieben. Das so erhaltene Produkt ist nach Trocknung an der Luft sehr feinkörnig und leicht in heißer verdünnter Schwefelsäure löslich, wobei sich als titrimetrisches Oxydationsmittel geeignete Lösungen von Sulfatocersäure $H_2Ce(SO_4)_3$ bilden.

Résumé—On décrit la préparation de l'hydroxyde cérique par précipitation contrôlée cinétiquement, en utilisant l'hydrolyse de l'urée et la réaction avec l'hexanitratocérate d'ammonium. Le produit ainsi obtenu, séché à l'air, se présente en particules fines et est aisément soluble en acide sulfurique dilué chaud, formant des solutions d'acide sulfatocérique $H_2Ce(SO_4)_3$; celles-ci sont utilisées comme oxydant pour titrages.

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