

80, copper(II) 28, iron(III) 2, chloride 8000, bromide 1790, fluoride 1350, nitrate 4625, acetate 4620, phosphate 1285, EDTA 4350, sulphate 900 and iodide 8.

The method has been successfully utilized for the determination of Os(VIII) in synthetic mixtures corresponding to syserkite.

The proposed method offers the advantages of simplicity, rapidity and sensitivity without the need for extraction or heating. The sensitivity of the proposed method is found to be more than that of other spectrophotometric reagents for Os(VIII) like 2-mercaptobenzimidazole⁶, 2-mercaptobenzothiazole⁷, 1-carbamidino-3-methyl-5-pyrazolene⁸, acenaphthenequinone monoxime⁹ and rubeanic acid¹⁰.

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Rapid Spectrophotometric Determination of Ce(IV), As(III) & Nitrite with Promethazine Hydrochloride

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Promethazine hydrochloride is proposed as a new reagent for the spectrophotometric determination of cerium(IV), arsenic(III) and nitrite. The reagent forms red-coloured product with Ce(IV) instantaneously in 3.9-5.3M phosphoric acid. The red colour exhibits absorption maximum at 518 nm with molar absorptivity 1.006×10^4 litre mole⁻¹ cm⁻¹. Beer's law is valid over the concentration range 0.40-15.6 ppm of Ce(IV). Foreign ions which commonly accompany Ce(IV) do not interfere. Arsenic(III) and nitrite are indirectly determined.

SANKE GOWDA *et al.*^{1,2} proposed promethazine hydrochloride (PH), 10-[2-dimethylaminopropyl] phenothiazine hydrochloride as redox indicator in vanadimetry¹ and cerimetry². The authors have now investigated the colour reaction between PH and cerium(IV) and proposed PH as a sensitive reagent for the spectrophotometric determination of Ce(IV), As(III) and nitrite. The proposed method

offers the advantages of simplicity, sensitivity and no need for extraction.

Stock solutions of cerium(IV) sulphate in 0.5M sulphuric acid, sodium arsenite (prepared from arsenic trioxide) and sodium nitrite were prepared and standardized by the known methods. A 0.2% solution of PH was prepared in doubly distilled water and stored in an amber bottle in a refrigerator. Solutions of diverse ions of suitable concentrations were prepared using analytical grade reagents.

Beckman model DB spectrophotometer with stoppered silica cells of 1 cm optical path was used for absorbance measurements.

Procedure for the determination of Ce(IV) — An aliquot of the stock solution containing 10-390 µg of Ce(IV), 11 ml of 10M phosphoric acid and 4 ml of 0.2% PH solution were taken and the solution diluted to 25 ml with doubly distilled water. The absorbance was measured at 518 nm against a corresponding reagent blank prepared in the same manner. The amount of cerium was then deduced from the standard calibration curve.

Procedure for the determination of arsenic(III) — Aliquots of 0.5, 1.0, 1.5, 2.0 6.0 ml of arsenic(III) solution (3.75-60 µg) were taken in twelve 25 ml volumetric flasks. A thirteenth 25 ml flask was used for a simultaneous blank determination. 2 ml of 2.5M sulphuric acid, 0.5 ml of osmium(VIII) (1.2 µg) and 2 ml of 0.001M ceric sulphate were then added successively to each flask. After shaking the solution, 11 ml of 10M phosphoric acid and 4 ml of 0.2% PH solution were added and diluted to the mark with doubly distilled water, shaken thoroughly and the absorbances measured at 518 nm against distilled water. The amount of arsenic(III) in a test solution was then deduced from the standard calibration curve constructed by plotting the concentration of arsenic(III) versus the difference in the absorbance readings between the blank (in thirteenth flask) and the sample.

Procedure for the determination of nitrite — 2 ml of 2M sulphuric acid and 2 ml of 0.001M ceric sulphate were taken in each of twelve 25 ml volumetric flasks. 4 ml of sodium nitrite solution containing 1.25-43 µg of nitrite was transferred into each volumetric flask. After 5 min, 11 ml of 10M phosphoric acid and 4 ml of 0.2% PH were added and the volume made up to the mark with doubly distilled water. A blank containing all the reagents except nitrite was prepared in the thirteenth flask. All the thirteen solutions were shaken thoroughly and the absorbances measured at 518 nm against distilled water. The amount of nitrite in a test solution was deduced from the standard calibration curve constructed as described in the determination of As(III).

Cerium(IV) readily oxidizes PH to red coloured species in sulphuric or phosphoric acid medium. The maximum colour development takes place instantaneously at room temperature (27°) in 3.9-5.3M phosphoric acid solutions. The red coloured species assumed to be a radical cation shows maximum absorption at 518 nm and the absorbance remains constant for 20 min. The red colour is stable for about 5 min

in sulphuric acid. Hence 4.4M phosphoric acid is conveniently chosen for all further work. The reagent under similar conditions does not absorb around this wavelength thus promoting excellent analytical conditions. A 25-fold molar excess of PH is needed for the full development of the colour intensity. The absorbance values are insensitive to temperature in the range 10-50° but above 50° they gradually decrease. It was found that there was no appreciable change in the absorbance of the red-coloured species if the order of addition of reagents was changed.

Beer's law is obeyed from 0.40 to 15.60 ppm of cerium. The optimum concentration range evaluated by Ringbom's method³ is 1.60-14.86 ppm. The molar absorptivity is 1.006×10^4 litre mole⁻¹ cm⁻¹ at 518 nm. According to Sandell's expression, the sensitivity of the reaction is 0.0139 µg/cm². The errors are in general about ±2%.

The following amounts (µg/ml) of foreign ions which commonly accompany Ce(IV) were found to give less than 2% error in the determination of 8 µg/ml of Ce(IV): La(III) 4000, Pr(III) 4000, Nd(III) 4000, Gd(III) 4000, Dy(III) 4000, Ho(III) 4000, Er(III) 4000, Yb(III) 4000, Y(III) 4000, Tb(III) 4000, Os(VIII) 9, Ru(III) 4, Pd(II) 0.90, Pt(IV) 11, Ir(III) 10, Au(III) 0.25, Cu(II) 720, Ni(II) 800, Co(II) 880, Fe(III) 300, Ag(I) 18, Mg(II) 1600, Zn(II) 1518, Th(IV) 345, Zr(IV) 506, U(VI) 1028, As(V) 4000, chloride 7600, bromide 16640, iodide 0.80, fluoride 8177, sulphate 33, 360, acetate 7452, phosphate 6501, citrate 6400, tartrate 6233, nitrate 8432, thiosulphate 0.5 and EDTA 0.80.

It can be seen that many diverse cations especially lanthanides do not interfere in the determination of cerium(IV). The major advantage of this method is that PH can be used as a selective reagent for the determination of cerium(IV) in presence of large quantities of other lanthanides in readily attainable oxidation states without the use of masking agents. The sensitivity of the proposed method is more than that of other spectrophotometric reagents

like *o*-aminophenol⁴, chromotrope 2R⁵, salicyl-hydroxamic acid⁶ and sulphanilic acid⁷. This procedure has been successfully applied for the determination of Ce(IV) in misch metal.

Arsenic(III) and nitrite are indirectly determined. Arsenic(III) is quantitatively oxidized instantaneously to arsenic(V) by a known excess of ceric sulphate (20-80%) in 0.5M sulphuric acid medium containing 1.2 µg of osmium(VIII) which does not interfere under the experimental conditions. Nitrite is quantitatively oxidized to nitrate in 0.5M sulphuric acid in 5 min by a known excess of ceric sulphate (20-80%). The unreacted cerium(IV) is then determined colorimetrically by the proposed method. In the absence of other reducing substances, the reduction in the absorbance of the red colour produced by the fixed amount of ceric sulphate is directly proportional to the amount of arsenic(III) or nitrite present. Ce(III), As(V) and nitrate formed in the reaction are colourless and do not interfere. 0.15-2.4 µg/ml of arsenic(III) and 0.05-1.72 µg/ml of nitrite can be determined.

This method can be used for the spectrophotometric determination of micro quantities of other substances which are quantitatively oxidized by cerium(IV) in sulphuric acid to colourless, non-interfering products.

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