bear a linear relationship with the number of carbon atoms. This shows that the additive character of R_M is exhibited by these amino acids. The mechanism of separation of amino acids on silica gel-calcium oxalate layer is probably an adsorption process which is influenced mainly by (i) reversible hydrogen bond formation between the hydrogen atom of the amino group or carboxylic group and the oxygen atom of the adsorbent (silica gel and calcium oxalate), as has been proposed by Bark and Graham[4] for the TLC separation of phenols on polyamide impregnated layers of cellulose and (ii) a weak bond formation by the donation of lone pair of electrons by N of NH_2 group to the calcium ion, as suggested by Yasuda[5] for the TLC separation of aromatic amines on $CdSO_4$ impregnated silica gel plates. Besides the above two factors, the extent of adsorption is also influenced by steric and electronic effects of the substituent on the amino acid molecule. Further the possibility of hydrogen bonding between the N of NH_2 and the H of the hydrated silica in the same manner as proposed by Pires and Roseira[6] cannot be ruled out. Hence the movement of spots, i.e. R_F values depend upon the above adsorption factors and the solvation factor.

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Chlorpromazine Hydrochloride as a Spectrophotometric Reagent for Os(VIII) & Os(VI)

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Chlorpromazine hydrochloride forms a red coloured species with Os(VIII) and Os(VI) in hydrochloric acid medium. The red species exhibits absorption maximum at 530 nm. A twelve-fold molar excess of the reagent is necessary for the full development of colour intensity. The sensitivity of the reaction is 0·0152 $\mu g/cm^2$ for Os(VIII) and 0·0134 $\mu g/cm^2$ for Os(VI). Beer's law is valid over the concentration range 0·08-7·2 ppm for Os(VIII) and 0·04-8·6 ppm for Os(VI). The effects of acidity, time, order of addition of reagents, temperature, reagent concentration and diverse ions are reported.

CHLORPROMAZINE hydrochloride (CPH) was proposed for the spectrophotometric determination of Pd(II)[1]. A survey of chemical literature showed that no attempt has been made to study the reaction between CPH and osmium. In the present investigation, the reaction of CPH with Os(VIII) and Os(VI) has been studied. On the basis of the results CPH is proposed as a sensitive reagent for the rapid spectrophotometric determination of Os(VIII) and Os(VI).

Standard solution of Os(VIII) was prepared from osmium tetroxide (Johnson Matthey) in 0·2M sodium hydroxide. Standard solution of Os(VI) was prepared from potassium osmate (Johnson Matthey) in doubly distilled water. The stock solutions were further diluted to give standard solutions containing 30 $\mu g/ml$ of Os(VIII) or Os(VI). A 0·2% aqueous solution of CPH (May & Baker) was prepared and stored in the refrigerator. Solutions of acids and diverse ions of suitable concentrations were prepared using analytical grade reagents.

Procedure for the determination of Os(VIII) *or* Os(VI) — To an aliquot of the stock solution containing 2 to 180 μg of Os(VIII) or 1 to 215 μg of Os(VI) were added 12·5 ml of 6M hydrochloric acid and 3 ml of 0·2% CPH solution and the volume made up to 25 ml by adding doubly distilled water. The solution was mixed well and the absorbance was measured at 530 nm against a reagent blank prepared in the same way. The amount of osmium was then deduced from the standard calibration curve.

CPH is oxidized to red-coloured radical cation[2,3] by Os(VIII) or Os(VI) instantaneously in hydrochloric acid medium at room temperature (27°). Os(IV) does not react with CPH. The red radical cation formed in sulphuric acid medium is stable for only 10 min. Nitric acid medium cannot be used as it slowly oxidizes CPH. Maximum absorbance is achieved in 2·0-3·5M hydrochloric acid. The absorbance values remain constant for 1 hr in hydrochloric acid medium. Hence, a hydrochloric acid strength of 3M was chosen for all subsequent studies.

The red species exhibit maximum absorbance at 526-532 nm. The CPH and Os(VIII) or Os(VI) do not absorb around this wavelength. A 12-fold molar excess of the reagent is required to obtain the maximum intensity of colour. The absorbance readings are constant in the temperature range 4-50°. No change in the absorbance is observed when the order of addition of reactants was changed. Beer's law is valid over the concentration range 0·08-7·2 ppm of Os(VIII) or 0·04-8·6 ppm of Os(VI). The optimum concentration ranges as evaluated by Ringbom's method[4,5] are 0·8-7·0 ppm for Os(VIII) and 0·8-8·0 ppm for Os(VI). According to Sandell's expression, the sensitivities of the reaction are 0·0152 $\mu g/cm^2$ for Os(VIII) and 0·0134 $\mu g/cm^2$ for Os(VI). Sample solutions containing 4 $\mu g/ml$ of Os(VIII) or Os(VI) prepared by the standard procedure gave a relative error of $\pm 0·5\%$.

The following amounts ($\mu g/ml$) of diverse ions which commonly accompany Os(VIII) are found to give less than $\pm 2\%$ error in the determination of 4 $\mu g/ml$ of osmium: rhodium(III) 14, iridium(III) 13, platinum(IV) 12, gold(III) 0·5, ruthenium(III) 0·4, palladium(II) 0·4, nickel (II) 575, cobalt(II)

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-mercaptobenzimidazole[6], 2-mercaptobenzothiazole[7], 1-carbamidino-3-methyl-5-pyrazolene[8], acenaphthene-quinone monoxime[9] and rubeanic acid[10].

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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 $1·006 \times 10^4$ 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 vanadametry[1] and cerimetry[2]. 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