

Spectrophotometric Determination of Cerium(IV) with Triflupromazine Hydrochloride*

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Triflupromazine hydrochloride is proposed as a new reagent for the spectrophotometric determination of cerium(IV). The reagent forms red coloured species with cerium(IV) instantaneously in 2.5-4.0M phosphoric acid. The red species has absorption maximum at 503 nm with molar absorptivity 6.70×10^4 litre mole⁻¹cm⁻¹. A twenty-fold molar excess of the reagent is necessary for the full development of the colour intensity. Beer's law is valid over the concentration range 0.4-14.20 ppm of cerium(IV). The effects of acid concentration, time, temperature, order of addition of reagents, reagent concentration and diverse ions are reported. The proposed method offers the advantages of simplicity, selectivity, rapidity and without the need for extraction.

TRIFLUPROMAZINE hydrochloride (TPH), 10-[3 (dimethylamino)propyl]-2-trifluoromethylphenothiazine hydrochloride was proposed as a spectrophotometric reagent for the determination of palladium¹ and gold². The authors have now investigated the colour reaction between TPH and cerium(IV) and proposed TPH as a sensitive reagent for the spectrophotometric determination of cerium(IV).

Experimental

Apparatus: Beckman Model DB Spectrophotometer with stoppered silica cells of 1 cm optical path was used for absorbance measurements.

Reagents: Cerium(IV) sulphate solution: A stock solution of cerium(IV) sulphate was prepared in 0.5M sulphuric acid and standardised with arsenic(III) solution³.

TPH solution: A 0.2% solution of TPH was prepared in doubly distilled water and stored in an amber bottle in a refrigerator.

Diverse ions: Solutions of diverse ions of suitable concentrations were prepared using analytical grade reagents.

Procedure recommended for the determination of cerium(IV): Transfer the sample solution containing 10-355 μ g of cerium(IV), 7.5 ml of 10M phosphoric acid and 3 ml of 0.2% TPH solution to a 25 ml volumetric flask and dilute to the mark with doubly distilled water. Mix the solution and measure the absorbance at 503 nm against a corresponding reagent blank prepared in the same manner. Calculate the cerium concentration of the sample solution by means of a calibration curve.

Results and Discussion

Determination of cerium(IV): TPH is oxidised to red coloured species by cerium(IV) in sulphuric or phosphoric acid medium. The maximum colour development takes place instantaneously at room temperature (27°) in 2.5-4.0M phosphoric acid solutions (Table 1) as shown by the constancy of λ_{max} . The maximum colour intensity is not observed below 2.5M phosphoric acid. The reagent is slowly oxidised in phosphoric acid medium above 4.0M. The absorbance of the red coloured species assumed to be a radical cation remains constant for 35 min. The red colour is stable for about 5 min in sulphuric acid and unstable in hydrochloric acid. Nitric acid cannot be used as it oxidises TPH to a red coloured radical cation. Hence 3.0M phosphoric acid is conveniently chosen for all further work.

TABLE 1—EFFECT OF PHOSPHORIC ACID CONCENTRATION ON THE ABSORBANCE VALUES.

Amount of cerium(IV) taken=4.5 μ g/ml
 λ_{max} =503 nm.

Phosphoric acid M	Absorbance readings
1.00	0.1805
2.00	0.2007
2.50	0.2218
3.00	0.2218
3.50	0.2218
4.00	0.2218
4.50	0.2366
5.00	0.2596

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Absorption spectra. The absorption spectra of the red species and TPH are shown in Fig. 1. The phosphoric acid concentration in both the cases is 3M. The maximum absorbance of the red species is found at 500-506 nm. The reagent under similar conditions does not absorb around this wavelength thus promoting excellent analytical conditions. The molar absorptivity is 6.70×10^3 litre mole⁻¹cm⁻¹ at the absorption maximum of 503 nm. According to Sandell's expression, the sensitivity of the reaction is 0.020 µg/cm².

excess of TPH is needed for completeness of the reaction. The absorbance is not affected by temperature in the range 7-50°. Above 50° the absorbance gradually decreases with the rise of temperature.

Calibration and range. Beer's law is obeyed from 0.5 to 14.2 ppm of cerium at wavelengths, 500, 503, 505 and 510 nm. The optimum range as evaluated by Ringbom's method is 1.2-13.70 ppm. The errors are in general about ± 2%.

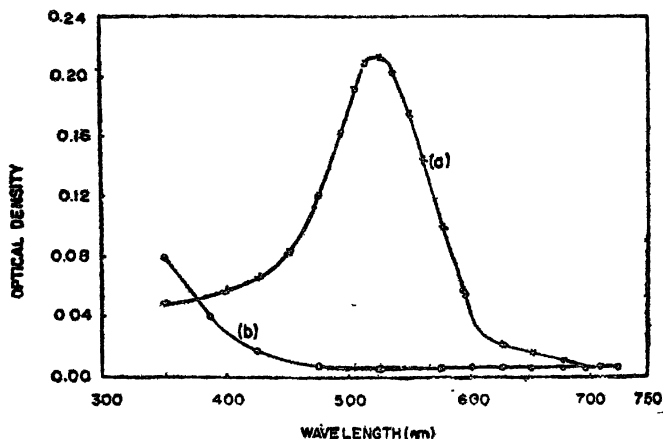


Fig. 1. Absorption spectrum of (a) red radical of TPH, (b) TPH. [TPH]= 6.5×10^{-4} M.

Order of addition of reagents. It was found that there was no appreciable change in the absorbance or in colour intensity of the red species if the order of addition of reagents was changed.

Effect of reagent concentration. The effect of reagent concentration was investigated by measuring the absorbance at 503 nm of solutions containing 4.5 ppm of cerium(IV) and varying the amount of reagent. The results are given in Table 2. A 20-fold molar

Effect of diverse ions. In order to assess the possible analytical applications of the reaction, the effects of some ions which often accompany cerium were studied. For these studies different amounts of ionic species were added to 175 µg of cerium contained in 25 ml volumetric flask and the colour was developed as outlined in the procedure. The following amounts (µg/ml) of foreign ions were found to give less than 2% error in the determination of 7 µg/ml of cerium(IV): La(III) 4000, Pr(III) 4000, Nd(III) 4000, Gd(III) 4000, Dy(III) 4000, Ho(III) 4000, Er(III) 4000, Yb(III) 0.0, Y(III) 4000, Tb(III) 4000, Os(VIII) 9, Ru(III) 6, Pd(II) 1.0, Pt(IV) 15, Ir(III) 10, Au(III) 0.3; Co(II) 290, Cu(II) 626.4, Ni(II) 571.7, Fe(III) 300, Ag(I) 12, Mg(II) 1500, Zn(II) 1619.2, Th(IV) 5, Zr(IV) 506, U(VI) 2100, As(V) 4000, chloride 8000, bromide 10400, iodide 0.16, fluoride 9086, sulphate 760, acetate 6624, phosphate 7318, citrate 7200, tartrate 5342.9, nitrate 8000, thiosulphate 0.6 and EDTA 0.50.

TABLE 2—EFFECT OF TPH CONCENTRATION ON THE ABSORBANCE VALUES

Amount of cerium(IV) taken = 4.5 µg/ml at 3.0M H₃PO₄, λ_{max} = 503 nm.

Molar excess of TPH	Absorbance readings
5.0	0.1871
10.0	0.2007
15.0	0.2147
20.0	0.2218
25.0	0.2218
30.0	0.2218
35.0	0.2218
40.0	0.2220
50.0	0.2220

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 TPH 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 *o*-aminophenol², salicylhydroxamic acid³ and

sulphanilic acid⁶ which have been proposed as sensitive spectrophotometric reagents for cerium. The sensitivity of the present method is less than that of *o*-tolidine⁷, diantipyrynyl *p*-nitrophenyl methane⁸, xylenol orange⁹, *p*-aminoacetophenone¹⁰ and phenyl anthranilic acid¹¹ which are used for the determination of cerium.

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