

Determination of Fe(II)-Fe(III) & of Fe(II)-U(IV) in Binary Mixtures by Ce(IV) & V(V) in Phosphoric Acid Medium

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Fe(II) can be estimated with Ce(IV) sulphate or sodium vanadate using cacotheline as indicator in H_3PO_4 (10-11M). The method has been extended for the estimation of Fe(III) after its reduction by $SnCl_2$ in HCl (0.5-1.5M). The mixtures of Fe(II) and Fe(III) and also Fe(II) and U(IV) have also been analysed.

THE use of phosphoric acid medium in the potentiometric study of the reaction between Fe(II) and vanadate was made by Gopala Rao and Dikshitulu¹. So far vanadate has not been used for the determination of Fe(III) after reduction with $SnCl_2$. U(VI) was determined with vanadate after prior reduction with excess Fe(II) both potentiometrically and visually². These observations led us to develop a method for the estimation of Fe(II) in its binary mixtures with Fe(III) and U(IV) by vanadate or ceric sulphate in phosphoric acid medium using cacotheline and ferroin as indicators.

All the reagents used, unless otherwise stated were of AR (BDH) grade. Cacotheline solution used (0.2%, wt/v) was of 99-99.5% purity³. Mohr's salt (0.1N) was prepared in 0.25M sulphuric acid. Ceric sulphate (0.1N) was prepared in 0.5M sulphuric acid. Sodium vanadate solution (0.1N) was prepared in boiled out distilled water. U(IV) was prepared by reduction of U(VI) in Jones reductor and then standardized according to the method given by Gopala Rao and coworkers⁴.

Determination of Fe(II)—Through 40 ml of phosphoric acid (10M) carbon dioxide was passed for 10 min. Then Mohr's salt solution (5 ml, 0.1N) and 0.5 ml indicator were added to the titration vessel and the titration carried with vanadate or ceric sulphate dropwise near the end-point to a sharp colour change of pink to yellow, while continuing the passage of carbon dioxide. The average error was found to be $\pm 0.30\%$.

Determination of Fe(III)—An aliquot (3 ml, 0.1N) of Fe(III) solution was taken in a titration vessel and HCl added to maintain an overall acidity of 1.0N in a total volume of 15 ml. Fe(III) was reduced with $SnCl_2$ after heating to 80-90°, 0.5 ml cacotheline was added when the yellow colour of Fe(III) almost disappeared and $SnCl_2$ further added until a pink colour was obtained, indicating the presence of excess of $SnCl_2$. The excess stannous was removed by adding ceric sulphate to the colour change of pink to yellow. Then the solution was cooled to room temperature and after passing carbon dioxide for 10 min and adding phosphoric acid the titration was carried with ceric sulphate as in case of Fe(II). The procedure for the estimation of Fe(III) with vanadate is the same as that with ceric sulphate except that the excess stannous is removed by adding ceric sulphate and not by adding vanadate. V(IV) pro-

TABLE 1—ESTIMATION OF Fe(II) AND Fe(III) WITH VANADATE OR CERIC SULPHATE

Fe(II), mg		Error (%)	Fe(III), mg		Error (%)
Taken	Found		Taken	Found	
SODIUM VANADATE					
28.80	28.70	-0.3462	6.40	6.42	+0.3124
22.50	22.56	+0.2728	11.10	11.07	-0.2703
17.18	17.25	+0.4074	19.20	19.27	+0.3646
11.50	11.47	-0.2550	25.46	25.50	+0.1572
5.68	5.67	-0.1762	32.10	31.98	-0.3739
CERIC SULPHATE					
22.10	22.18	+0.3620	6.45	6.472	+0.3410
17.50	17.44	-0.3530	12.80	12.76	-0.3125
29.20	29.23	+0.1028	3.48	3.47	-0.3617
11.75	11.80	+0.4255	19.40	19.44	+0.2062
5.919	5.902	-0.2939	24.78	24.72	-0.2422

duced in this case will interfere in the later part of the estimation in phosphoric acid medium. The average error was found to be $\pm 0.96\%$.

In a binary solution containing Fe(II)+Fe(III), Fe(II) was determined as described above. In another aliquot total Fe(III)+Fe(II) was determined after Fe(III) was reduced with $SnCl_2$ as described above. By subtracting the amount of Fe(II) obtained in the first case from the total, the amount of Fe(III) present was obtained. A few typical results are presented in Table 1.

Determination of Fe(II) and U(IV) in mixtures:

(i) *With sodium vanadate*—Enough phosphoric acid was taken so that the overall acidity was 10M when diluted to 40 ml. Carbon dioxide was passed through phosphoric acid for 10 min. To this was added a solution containing Fe(II)+U(IV) followed by 0.5 ml cacotheline were added and the titration carried out with vanadate to the appearance of yellow colour. The contents were then diluted with water to have phosphoric acid concentration of 7M. To this was added 1 drop of ferroin (0.025M) and the titration carried out with vanadate to the appearance of stable bright blue colour. The amount of vanadate consumed in the two titrations using cacotheline end-point and the ferroin end-point was equal to the total amount of U(IV) and V(III) produced during the titration of Fe(II) with vanadate. The equivalent of the latter is given by the amount of vanadate consumed up to cacotheline end-point. Hence the amount of U(IV) is computed from the two. A few typical results are presented in Table 2.

(ii) *With ceric sulphate*—In one aliquot Fe(II) was determined in phosphoric acid medium as given above. In a second aliquot the total of Fe(II) and U(IV) was determined under the conditions given by Birnbaum and Edmonds⁵ for the estimation of U(IV) with ceric sulphate. From the two results the amount of U(IV) was computed. A few typical results are presented in Table 2.

The method described for Fe(II) determination with ceric sulphate or sodium vanadate has the advantage that oxalate, tartrate, citrate, methanol, As(III), U(IV), Hg_2^{2+} and chloride do not interfere.

TABLE 2—ESTIMATION OF Fe(II) AND U(IV) WITH VANADATE OR CERIC SULPHATE

Fe(II), mg		Error (%)	U(IV), mg		Error (%)
Taken	Found		Taken	Found	
SODIUM VANADATE					
28.80	28.70	-0.3474	20.80	20.73	-0.3365
40.30	40.20	-0.2484	11.10	11.13	+0.2703
51.80	51.65	-0.2896	5.25	5.26	+0.1908
5.90	5.92	+0.3389	33.70	33.60	-0.2967
12.48	12.52	+0.3204	27.68	27.60	-0.2890
CERIC SULPHATE					
5.70	5.68	-0.3508	37.50	37.60	+0.2667
10.60	10.63	+0.2830	26.20	26.12	-0.3053
17.10	17.04	-0.3509	17.12	17.18	+0.3405
23.50	23.44	-0.2553	11.40	11.37	-0.2631
28.75	28.83	+0.2783	2.93	2.924	-0.2047

V(III) interferes in the estimation of Fe(II) with vanadate in sulphuric acid medium, whereas it does not interfere in the present case. Oxalate, As(III) and U(IV) interfere in the estimation of Fe(II) with ceric sulphate in sulphuric acid medium, but in the present case they do not interfere.

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Extraction & Spectrophotometric Determination of Pd(II) with 2'-Hydroxy-4-methoxy-5'-methylchalkone Oxime

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A fast and selective procedure is described for the extraction and direct spectrophotometric determination of Pd(II) using 2'-hydroxy-4-methoxy-5'-methylchalkone oxime (HMMCO) in isobutanol. The Pd(II)-HMMCO complex is quantitatively extracted at pH 0.5-2.5 and obeys Beer's law in the concentration range 1.0-30.0 μg of Pd(II) per ml of isobutanol at 380 nm. The complex having molar absorptivity 3.38×10^3 is highly stable. Palladium can be clearly separated and determined in the presence of large number of ions.

THE use of 2'-hydroxy-4-methoxy-5'-methylchalkone oxime (HMMCO) for the simultaneous gravimetric determination of Pd(II), Cu(II) and Ni(II) has been described by us earlier¹. The study of liquid-liquid extraction of less common metals in our laboratory showed that Pd(II) can be quantitatively extracted with HMMCO in the pH range 0.5-2.5. This has now been employed for the spectrophotometric determination of Pd(II).

The extraction of Pd(II) with several oximes are known²⁻⁶. Amongst many oximes the quantitative extraction with resacetophenone oxime⁴ required 5 hr whereas with the present oxime it takes 8-10 min for quantitative extraction. In addition a number of other chelating agents⁷ were also tried as extractants.

The oxime was synthesized from *p*-cresol as reported earlier⁸. About 0.002M HMMCO in isobutanol was used for extraction studies.

A stock solution of palladium perchlorate was prepared by dissolving palladium chloride (~ 0.98 g, Johnson-Matthey) and standardized by gravimetric methods^{1,9}. The solutions of desired concentrations were prepared by appropriate dilution.

General procedure—The pH of a solution containing 100 μg of Pd(II) was adjusted 1.0-2.0 with perchloric acid and sodium hydroxide, the final volume being 25 ml. The solution was shaken with 10 ml of 0.002M HMMCO in isobutanol for 10 min. The organic layer was separated and the absorbance was measured at 380 nm, the wavelength of maximum absorbance, against the reagent blank. Pd(II) present was computed from the calibration curve, as usual.

The molar absorptivity of the complex was 3.38×10^3 . The sensitivity by Sandell's definition is 0.020 $\mu\text{g}/\text{cm}^2$. The Pd(II)-HMMCO system obeyed Beer's law over the concentration range 1-30 μg of Pd(II) per ml of isobutanol. Most suitable working range according to Ringbom plot was found to be 10-20 μg of Pd(II) per ml of isobutanol. Pd(II)-HMMCO complex is stable for 5 days.

The quantitative extraction of Pd(II) is possible with reagent concentration 2×10^{-3} - 2.5×10^{-3} M over the pH range of 0.5-2.5. The extraction decreases above pH 3.0 for all concentration of the reagent.

The composition of the extractable species was found to be 1:2 (Pd-HMMCO) by the plot of $\log D_{\text{Pd}}$ versus $\log C$ (HMMCO concentration).

Amongst the various non-aqueous solvents, viz. methyl isobutyl ketone, *n*-butanol, isoamyl alcohol, cyclohexanol, ethyl acetate, chloroform and benzene, isoamyl or isobutyl alcohol were found to be most efficient.

Many foreign ions were tested for interferences. The tolerance limit was set as the amount of foreign ion needed to cause $\pm 2\%$ error in the recovery of Pd(II). Many ions are tolerable whose tolerance limit are given in Table 1. The tolerance of Hg(II) is hundred and fifty-fold, whereas that of Rh(III) is three-fold. The strong interfering ions include Fe(III), Ru(III), ZrO(II), citrate, tartarate and EDTA.

The absorbance obtained from eight determination of 100 μg of Pd(II) was 0.500 ± 0.005 . The relative mean deviation and standard deviation have