

# **Titrimetric Determination of Manganese(II), Cobalt(II) and Nickel(II) with 1,2-Diaminocyclohexanetetraacetic Acid**

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**1,** 2-Diaminocyclohexanetetraacetic acid (DCTA), has been used previously for the determination of iron(III)<sup>1,2</sup>, vanadium(IV)<sup>3</sup> and thorium(IV)<sup>4</sup>. In the present communication, its use has been extended to the visual and/or spectrophotometric determination of manganese(II), cobalt(II) and nickel(II).

## **Experimental**

**Reagents:** DCTA (Koch-Light), manganese(II) sulphate tetrahydrate, cobalt(II) sulphate heptahydrate (BDH, AnalaR), nickel(II) sulphate hexahydrate, succinimide (E. Merck), thymolphthalexone (Koch-Light), catechol violet (BDH) and pyrogallol red (SDS) were used as such. All other chemicals used were of guaranteed purity. Double distilled water was used throughout.

**Solutions:** The solutions of DCTA (0.005-0.05 *M*), manganese(II) sulphate, cobalt(II) sulphate, nickel(II) sulphate ( $5 \times 10^{-3}$  *M*) and manganese ore (0.2 g/100 ml) were prepared and standardized or the manganese content estimated by the reported methods<sup>5-7</sup>.

**Apparatus:** The pH of the solutions was measured with an ELICO model LI-10 pH meter. The spectrophotometric titrations were carried out using Specord UV VIS spectrophotometer and Beckman DU spectrophotometer using 1 cm cells.

**Visual determination of manganese(II):** The solutions of ascorbic acid (~1 ml, 0.1%), tartaric acid (~1 ml, 0.1%), thymolphthalexone indicator (10 drops, 0.05%) and sodium carbonate-hydrochloric acid buffer (~3 ml) of pH 9.75-10.50 were added to an aliquot (0.5-10 ml) of manganese(II) sulphate solution. The content were titrated with standard DCTA solution to a colour change from blue to almost colourless.

An aliquot (0.5-10 ml) of manganese(II) sulphate solution and solutions of triethanolamine (~1 ml, 8%), hydroxylamine hydrochloride (~1 ml, 2%) and catechol violet indicator (1 drop, 0.1%) were titrated with standard DCTA solution in the pH range 9.75-10.50 to a colour change from bluish green to violet. The pH was adjusted with ammonia-ammonium chloride buffer (~3 ml) of required pH.

**Visual determination of cobalt(II):** An aliquot (0.5-5 ml) of cobalt(II) sulphate solution containing 10% succinimide solution (~5 ml) or pyrogallol red (10 drops of saturated solution in 50% ethanol) indicator was titrated with standard DCTA solution

after adding ammonia-ammonium chloride buffer (2-5 ml) of pH 9.5-11.0 and 9.75-10.5 to a sharp colour change from blue to colourless and from blue to red, respectively.

**Visual determination of nickel(II):** An aliquot (0.5-5 ml) of nickel(II) sulphate solution containing solutions of pyrogallol red (10 drops) and ascorbic acid (~5 ml, 0.1%) was titrated with standard DCTA solution after adding ammonia-ammonium chloride buffer (~5 ml) of pH 10.0-10.1 to a sharp colour change from blue to violet.

An aliquot of manganese(II), cobalt(II) or nickel(II) sulphate solution containing calcium(II), strontium(II) or barium(II) ions (2 ml,  $5 \times 10^{-3}$  *M*) was treated with potassium fluoride solution (3-5 ml, 1.2%) to mask these ions and the content was titrated against standard DCTA solution after buffering to proper pH. The interference due to copper(II) was dealt with by adding required amount of thiosulphate solution to an aliquot of these ions containing copper(II) solution. Lead(II) was removed by filtering off the precipitate of lead(II) sulphate formed by adding sulphuric acid (~1 ml, 0.5 *M*). The interference of mercury(II) (2 ml,  $5 \times 10^{-3}$  *M*) was dealt with by adding potassium iodide solution (~4 ml, 1%) before adding the buffer.

In the determination of manganese(II), the masking of silver(I), zinc(II), cadmium(II), cobalt(II) and nickel(II) ions (1 ml,  $5 \times 10^{-3}$  *M*) was carried out by adding potassium cyanide solution (3-4 ml, 1%) and hydroxylamine hydrochloride solution (~1 ml, 2%) to a solution of manganese(II) sulphate containing any of the above five metal ions. Iron(III) was removed by adding zinc oxide suspension to an aliquot of manganese(II) sulphate solution containing iron(III) ions. The iron(III) hydroxide so precipitated was filtered off and the resulting filtrate titrated as above after masking zinc(II) ions with potassium cyanide solution. An aliquot (5-10 ml) of manganese ore solution was titrated with DCTA according to the above procedure after the removal of iron(III) with zinc oxide suspension.

**Spectrophotometric determination of manganese(II) and cobalt(II):** An aliquot (1-2 ml) of cobalt(II) solution and succinimide (~0.5 g), or that of manganese(II) solution (1-5 ml), triethanolamine (~1 ml, 8% solution), hydroxylamine hydrochloride solution (~1 ml, 2%) and thymolphthalexone (10 drops) or catechol violet (1 drop) indicator was titrated with standard DCTA solution in the pH range 9.75-10.50 at 590, 625 or 680 nm, respectively (Fig. 1). The absorbance was measured after each small addition of DCTA solution, corrected for dilution and then plotted as a function of the volume of DCTA added. The equivalence point was obtained by extrapolating the straight lines (Fig. 2).

These titrations were repeated at least five times at each concentration level with and without adding foreign ions.

## Results and Discussion

A perusal of the results presented in Tables 1-5 suggests that DCTA reacts with manganese(II), cobalt(II) or nickel(II) in 1 : 1 molar ratio under the experimental conditions. The colour change at the end point in all these titrations is quite sharp indicating that there is no stepwise formation of successive complexes. The titration procedure is simple and consumes very little time. As little as 0.14, 0.13 and 0.13 mg of manganese(II), cobalt(II) and nickel(II), respectively can be quantitatively determined.

The blue, bluish green and blue complexes formed by manganese(II) with thymolphthalexone or catechol violet and by cobalt(II) with succinimide in the pH range 9.75-10.50 have maximum absorbance at  $\sim 625$ , 680 or 590 nm, respectively (Fig 1). The corresponding DCTA-metal complexes do not show

significant absorbance at these wave lengths. Since the DCTA-metal complex is stronger than metal-indicator complex under the experimental conditions, the colour of the latter disappears gradually as the equivalence point is approached in the titration of metal-indicator solution with DCTA. After the equivalence point, the absorbance remains almost constant (Fig. 2). The standard deviation in spectrophotometric titration is less than that in the visual method.

The spectrophotometric titration of nickel(II) is not carried out due to non-availability of a suitable indicator.

**Interferences:** Interfering effect of the metal ions depends primarily on the difference in conditional stability constants of the various metal ions present in the solution. In the present study, it is observed that manganese(II), cobalt(II) or nickel(II)

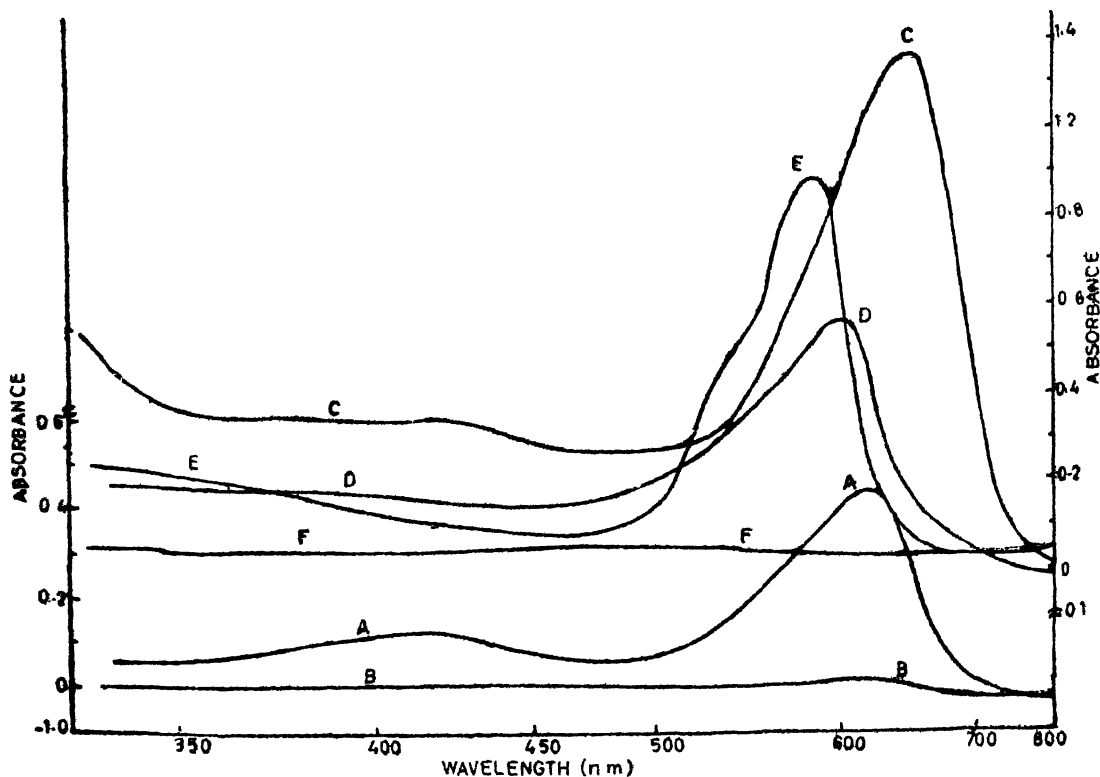


Fig. 1. Absorption spectra of metal ion - indicator complexes and DCTA-metal ion complexes.

- A:  $1.43 \times 10^{-3}$  M Manganese(II), 8% Triethanolamine, 2% Hydroxylamine hydrochloride, 0.05% Thymolphthalexone indicator, pH 10.00,  $1.32 \times 10^{-3}$  M DCTA.  
 B:  $1.43 \times 10^{-3}$  M Manganese(II), 8% Triethanolamine, 2% Hydroxylamine hydrochloride, 0.05% Thymolphthalexone, pH 10.00,  $1.32 \times 10^{-3}$  M DCTA.  
 C:  $1.43 \times 10^{-3}$  M Manganese(II), 8% Triethanolamine, 2% Hydroxylamine hydrochloride, 0.1% Catechol violet, pH 10.00.  
 D:  $1.43 \times 10^{-3}$  M Manganese(II), 8% Triethanolamine, 2% Hydroxylamine hydrochloride, 0.1% Catechol violet, pH 10.00,  $1.32 \times 10^{-3}$  M DCTA.  
 E:  $2.50 \times 10^{-3}$  M Cobalt(II), 0.5 g Succinimide indicator, pH 10.6.  
 F:  $2.50 \times 10^{-3}$  M Cobalt(II), 0.5 g Succinimide indicator,  $1.77 \times 10^{-3}$  M DCTA, pH 10.6; Path length 1 cm.

# NOTES

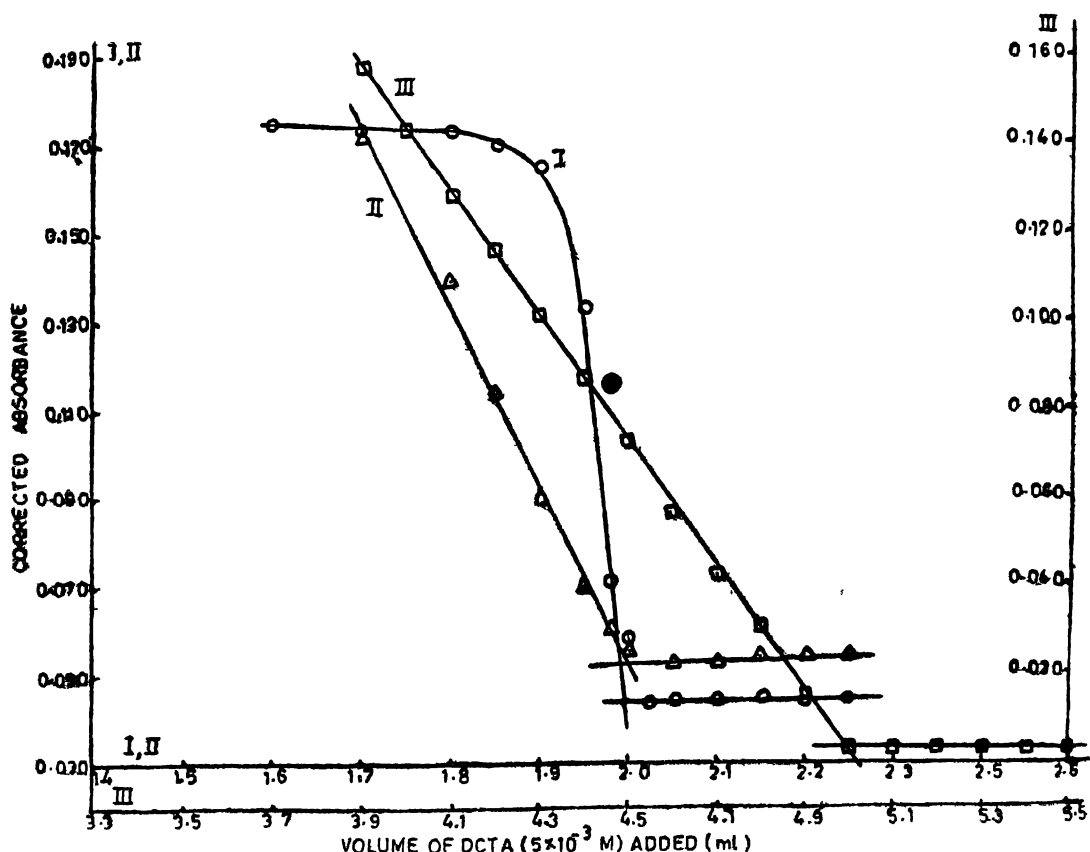


Fig. 2. Spectrophotometric titrations of metal ions with DOTA using metal chromic indicators.

Curve I and II : Titrations of manganese(II) (2.00 ml,  $5 \times 10^{-3}$  M) with DOTA using thymolphthalexone indicator at 625 nm (○—○) and catechol violet indicator at 680 nm (△—△).

III : Titration of cobalt(II) (5.00 ml,  $5 \times 10^{-3}$  M) with DOTA using succinimide indicator at 590 nm (□—□).

TABLE 1—VISUAL DETERMINATION OF MANGANESE(II) WITH DOTA IN PRESENCE OF VARIOUS IONS USING THYMOLPHTHALEXONE AND CATECHOL VIOLET INDICATORS

Ion added mg	Taken	Amount of manganese(II) mg		Standard deviation $\times 10^3$	
		Found using		Thymolphthalexone	Catechol violet
		Thymolphthalexone	Catechol violet		
	0.14	0.14	0.14	1.0	1.1
	1.87	1.87	1.87	1.0	0.9
	2.75	2.74	2.75	1.2	1.0
Ag <sup>+</sup>	1.85	0.69	0.68*	1.2	1.3
	17.57	1.79	1.80*	0.9	1.4
	45.95	2.84	2.88*	1.0	1.1
Zn <sup>2+</sup>	0.65	0.55	0.54*	1.0	1.2
	8.15	1.87	1.88*	1.1	1.3
	26.18	2.20	2.19*	1.2	1.0
Cd <sup>2+</sup>	0.84	0.41	0.41*	1.4	1.3
	19.64	1.92	1.90*	1.2	1.1
	50.53	2.47	2.46*	1.2	1.2
Ca <sup>2+</sup>	0.40	0.55	0.55*	1.2	1.3
	4.99	1.87	1.86*	0.9	1.4
	16.05	2.20	2.18*	1.0	1.1

(Table 1 contd.)

Sr <sup>2+</sup>	0.65	0.41	0.41*	0.41	1.0	0.9
	13.16	1.65	1.65*	1.65*	1.4	1.1
	39.89	2.47	2.48*	2.49*	1.8	1.2
Ba <sup>2+</sup>	0.67	0.27	0.27*	0.27*	1.4	1.2
	20.62	1.65	1.69*	1.69*	1.2	1.1
	61.75	2.47	2.49*	2.46*	1.2	1.0
Cu <sup>2+</sup>	0.47	0.41	0.41*	0.41*	1.0	0.8
	6.26	1.09	1.07*	1.08*	0.9	0.9
	14.30	1.24	1.22*	1.22*	1.0	1.2
Hg <sup>2+</sup>	5.50	1.51	1.50*	1.52*	1.4	1.0
	37.25	2.06	2.06*	2.08*	1.2	1.3
	95.30	2.60	2.61*	2.62*	1.0	1.2
Pb <sup>2+</sup>	3.09	0.82	0.82*	0.82*	1.4	1.3
	16.10	1.65	1.66*	1.67*	1.2	1.0
	93.17	2.47	2.48*	2.49*	0.9	1.1
Fe <sup>2+</sup>	0.56	0.55	0.55*	0.54*	1.0	1.3
	7.68	1.51	1.52*	1.52*	1.4	0.9
	26.53	2.61	2.63*	2.63*	1.3	1.1

\* After masking/removing the interfering ions.

TABLE 2—VISUAL AND SPECTROPHOTOMETRIC DETERMINATION OF COBALT(II) WITH DCTA IN PRESENCE OF VARIOUS IONS USING SUCCINIMIDE INDICATOR

Ion added mg	Amount of cobalt(II) mg		Standard deviation $\times 10^3$		
	Taken	Found	Visually	Spectrophotometrically	Spectrophotometrically
		Visually			
	0.15	0.15	0.15	1.2	0.2
	0.81	0.81	0.81	1.1	0.3
	1.47	1.46	1.47	1.2	0.4
Ag <sup>+</sup>					
	0.81	0.44	0.44	interferes	1.4
	2.69	1.47	1.45	interferes	1.8
	5.38	1.47	interferes	interferes	—
Ca <sup>2+</sup>					
	0.30	0.44	0.44*	interferes	1.4
	2.51	0.74	0.73*	interferes	1.4
	7.01	1.03	1.02*	interferes	1.3
Sr <sup>2+</sup>					
	0.88	0.59	0.59*	interferes	1.2
	6.57	0.88	0.88*	interferes	1.1
	21.91	1.47	1.46*	interferes	1.0
Ba <sup>2+</sup>					
	1.20	0.52	0.52	0.52	1.1
	3.43	1.47	1.46	1.47	1.0
	6.86	1.47	interferes	interferes	—
Cu <sup>2+</sup>					
	0.32	0.29	0.29*	interferes	1.2
	4.75	0.88	0.88*	interferes	1.2
	11.91	1.11	1.12*	interferes	1.3
Hg <sup>2+</sup>					
	1.25	0.37	0.37*	interferes	1.1
	12.50	0.74	0.73*	interferes	1.4
	40.20	1.18	1.18*	interferes	1.5
Pb <sup>2+</sup>					
	1.04	0.29	0.29*	interferes	1.2
	2.59	0.74	0.74*	interferes	1.0
	4.66	1.33	1.35*	interferes	1.3
La <sup>3+</sup>					
	1.04	0.44	0.44	0.44	1.2
	3.47	1.47	1.45	1.46	1.3
	6.94	1.47	interferes	interferes	—
S <sup>2-</sup>					
	0.20	0.37	0.37	0.37	1.4
	0.80	1.47	1.48	1.47	1.3
	1.60	1.47	interferes	interferes	—

\* After masking/removing the interfering ions.

TABLE 3—VISUAL DETERMINATION OF COBALT(II) AND NICKEL(II) WITH DCTA IN PRESENCE OF VARIOUS IONS USING PYROGALLOL RED INDICATOR

Ion added mg	Amount taken mg		Amount found mg		Standard deviation $\times 10^3$	
	Co <sup>2+</sup>	Ni <sup>2+</sup>	Co <sup>2+</sup>	Ni <sup>2+</sup>	Co <sup>2+</sup>	Ni <sup>2+</sup>
	0.15	0.15	0.15	0.15	1.2	1.3
	0.88	0.73	0.87	0.73	0.8	1.2
	1.47	1.47	1.46	1.45	1.1	1.1
Ag <sup>+</sup>						
	1.21	0.66	0.66	0.66	1.2	1.2
	2.69	1.47	1.47	1.45	1.3	1.3
	5.38	1.47	1.47	interferes	—	—

(Table 3 contd.)

Ca <sup>2+</sup>	0.20	0.29	0.44	0.28*	0.45*	1.0	1.2
	1.50	0.44	0.81	0.43*	0.82*	0.9	1.3
	4.01	0.59	1.25	0.58*	1.26*	1.4	1.4
Sr <sup>2+</sup>	1.09	0.74	0.51	0.73*	0.51*	1.2	1.1
	8.76	1.18	0.66	1.18*	0.66*	0.9	1.4
	19.71	1.33	1.10	1.32*	1.11*	1.3	1.3
Ba <sup>2+</sup>	1.20	0.52	0.29	0.52	0.29	1.2	1.1
	3.43	1.47	1.47	1.46	1.45	1.1	1.2
	6.86	1.47	1.47	interferes	interferes	—	—
Cu <sup>2+</sup>	0.40	0.37	0.15	0.37*	0.15*	1.1	1.2
	0.87	0.81	0.88	0.82*	0.88*	1.0	1.1
	11.92	1.11	1.03	1.10*	1.04*	1.1	1.4
Hg <sup>2+</sup>	1.25	0.37	0.44	0.37*	0.44*	1.1	1.1
	11.28	0.66	1.17	0.66*	1.18*	1.0	1.2
	32.60	0.96	1.32	0.97*	1.38*	1.1	1.4
Pb <sup>2+</sup>	4.14	1.18	0.37	1.19*	0.37*	1.3	1.2
	4.40	1.25	0.78	1.24*	0.72*	1.5	1.4
	4.92	1.40	1.39	1.42*	1.41*	1.4	1.5
S <sup>2-</sup>	0.20	0.37	0.15	0.36	0.15	1.1	1.4
	0.80	1.47	1.47	1.46	1.49	1.4	1.3
	1.60	1.47	1.47	interferes	interferes	—	—
PO <sub>4</sub> <sup>3-</sup>	3.60	0.22	0.59	0.22	0.59	1.3	1.1
	47.88	1.47	0.88	1.46	0.88	1.2	1.1
	236.89	1.47	1.32	interferes	1.33	—	1.3

\* After masking/removing the interfering ions.

TABLE 4—VISUAL DETERMINATION OF A BINARY MIXTURE OF MANGANESE(II) AND COBALT(II) WITH DCTA USING THYMOLPHTHALEXONE AND CATECHOL VIOLET INDICATORS

Indicator	Amount taken, mg		Amount found, mg		Standard deviation $\times 10^3$	
	Mn <sup>2+</sup>	Co <sup>2+</sup>	Mn <sup>2+</sup>	Co <sup>2+</sup>	Mn <sup>2+</sup>	Co <sup>2+</sup>
Thymol-phthalexone	0.82	0.59	0.83	0.59	1.4	1.2
	1.65	1.18	1.66	1.18	1.2	1.3
	2.47	2.47	2.44	2.50	1.1	1.1
Catechol violet	0.27	0.59	0.27	0.59	1.1	1.2
	1.65	0.88	1.64	0.88	1.2	1.0
	2.61	1.18	2.63	1.19	1.4	1.3

\* From difference in titration values in presence and absence of the masking agent.

TABLE 5—VISUAL DETERMINATION OF A BINARY MIXTURE OF MANGANESE(II) AND NICKEL(II) WITH DCTA USING THYMOLPHTHALEXONE AND CATECHOL VIOLET INDICATORS

Indicator	Amount taken mg		Amount found mg		Standard deviation $\times 10^3$	
	Mn <sup>2+</sup>	Ni <sup>2+</sup>	Mn <sup>2+</sup>	Ni <sup>2+</sup>	Mn <sup>2+</sup>	Ni <sup>2+</sup>
Thymol-phthalexone	0.55	0.29	0.55	0.28	1.1	1.3
	1.65	0.88	1.66	0.88	1.0	1.1
	2.75	1.18	2.73	1.19	1.2	1.0
Catechol violet	0.82	0.59	0.82	0.58	1.2	1.4
	1.37	0.88	1.36	0.88	1.0	0.8
	2.75	1.47	2.77	1.46	1.3	0.9

\* From difference in titration values in presence and absence of the masking agent.

is determined quantitatively in presence of 100 times as much of lithium, sodium, potassium, fluoride, chloride, iodide, nitrate and sulphate ions. Equimolar amount of barium(II) ions is bearable in these titrations except when thymolphthalexone is used as indicator in the determination of manganese. Upto 100 times excess of phosphate does not interfere under the experimental conditions except in the determination of cobalt(II) employing pyrogallol red as indicator where only 20 times excess is bearable. Upto 100 times excess of thiosulphate does not interfere in these titrations except when succinimide is used as indicator in the estimation of cobalt(II) where even its traces interfere seriously. Equimolar amount of silver(I) ions is bearable in visual estimation of cobalt(II) or nickel(II) though a precipitate of silver hydroxide is formed. However, it interferes in the determination of manganese(II). Lanthanum(III) interferes except in titration using succinimide as indicator in the determination of cobalt(II) where even its equimolar amount causes no interference.

Magnesium(II), nickel(II) and cobalt(II) ions are co-titrated with manganese(II) quantitatively and thus interfere in these titrations. The amount of DCTA used is exactly the same as that required for the sum of any of these ions present and manganese(II). However, the titration is not possible in the presence of higher amounts of cobalt(II) and nickel(II) because the end point can not be detected accurately due to their intense colour. Calcium(II), strontium(II), copper(II), mercury(II), lead(II), zinc(II), aluminium(III), iron(III), chromium(III) and thorium(IV) interfere seriously in these titrations.

In visual titrations, calcium(II), strontium(II) and barium(II) ions are masked with potassium fluoride solution as their slightly soluble fluorides do not interfere. Copper(II) and mercury(II) are masked with thiosulphate\* and potassium iodide, respectively when non-interfering copper(II)-thiosulphate complex or  $[HgI_4]^{2-}$  complex ion is formed. Lead(II) is precipitated out as its sulphate with 0.5 M sulphuric acid and removed by filtration.

In the estimation of manganese(II), the masking of silver(I), zinc(II), cadmium(II), cobalt(II) and nickel(II) is effected with aqueous potassium cyanide solution and hydroxylamine hydrochloride when the corresponding stable cyano-complexes of these ions are formed. Potassium cyanide does not form a complex with manganese(II) under the experi-

mental conditions. Since hydroxylamine hydrochloride is already present in the titrations using catechol violet as indicator, addition of more of this reagent is not required. The method is thus utilized for the analysis of a binary mixture of manganese(II) with cobalt(II) or nickel(II). The interference due to iron(III) is removed by adding zinc oxide suspension and filtering off the precipitated iron(III) hydroxide. The excess zinc oxide is masked with potassium cyanide.

The method is of particular significance for the determination of manganese(II) in its ore. The method is simple and no vigorous shaking and heating (80-90°) are required unlike the conventional potassium permanganate titration method. Iron(III) is removed before estimating manganese(II) according to the procedure mentioned above. Other constituents of the manganese ore do not interfere in the titration. Manganese(II) is thus estimated in manganese ore with  $\pm 0.55\%$  error (Table 6).

TABLE 6—DETERMINATION OF MANGANESE(II) IN MANGANESE ORE WITH DCTA USING THYMOL-PHTHALEXONE AND CATECHOL VIOLET INDICATORS

Reported method	Manganese(II) found mg		% Error	
	Thymol-phthalexone	Catechol violet	Thymol-phthalexone	Catechol violet
392.97	390.79	390.81	-0.55	-0.55
390.32	391.42	391.98	+0.31	+0.45
389.06	390.88	390.52	+0.47	+0.38

An attempt to mask other interfering ions with common masking agents is not successful.

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