TABLE 1 — RESULTS OF ESTIMATION OF Mn(II) WITH SODIUM BENZILATE

Amount of Mn(II) (mg)		Error (%)
Volumetric method using bismuthate	Present method	
10·00	10·10	+1·00
13·55	13·49	−0·44
21·95	21·95	0·00
32·53	32·43	−0·30
48·33	48·59	+0·53
55·83	55·42	−0·73
66·08	66·24	+0·24
74·52	74·36	−0·21
79·10	79·45	+0·44

gravimetric method for the estimation of Mn(II) using sodium benzilate as precipitating reagent is being reported in this note.

Manganous sulphate (GR, E. Merck) and benzilic acid, $(C_6H_5)_2C(OH)COOH$ (E. Merck) were used. Thermogravimetric analysis was carried out on a derivatograph (MOM).

Sodium benzilate when mixed with Mn(II) gave an instantaneous pale-pink precipitate of Mn(II)-benzilate. It was washed and dried at 120° and analysed [Found: C, 61·45; H, 4·78; Mn, 9·92. Required for $MuBz_2.2H_2O$ [where Bz = $(C_6H_5)_2C(OH)COO^-$]: C, 61·65; H, 4·88 and Mn 10·10%]. On heating the sample (100 mg) in the derivatograph at a rate of 5°/min decomposition started at 156°, the maximum decomposition occurring around 280°. The calculated and observed metal oxide (MnO) were 13·0 and 13·9 respectively for the composition $MnBz_2.2H_2O$. The magnetic moment (Gouy method, ~30°) of the solid complex has been found to be 5·88 BM which is only slightly lower than the value expected theoretically[2] for a d^5 system (5·92 BM) on the basis of spin-only formula. The infrared spectrum (Perkin-Elmer model 337) of the solid complex in nujol shows a peak around 815 cm^{-1} which is absent in free benzilic acid. This band may be due to the presence of coordinated water in the solid complex. This finds support from the earlier studies[3-5] on aquo coordinated complexes which show bands between 795 and 910 cm^{-1} for the coordinated water. It is possible that $MnBz_2.2H_2O$ has octahedral symmetry.

The insolubility of $MnBz_2.2H_2O$ in water and the constant composition when dried at 110-20° are the main advantages of sodium benzilate as the precipitating agent.

Procedure for the determination of Mn(II) — Aqueous sodium benzilate (0·2*M*) was added gradually with stirring to a solution of Mn(II) (10-80 mg) till the precipitation was complete. The optimum *p*H range was 3·2-5·4. The precipitate was filtered, washed thoroughly with water, 50% ethanol, dried at 110°-20° and weighed. The manganese content was calculated on the basis of formula $Mn[(C_6H_5)_2C(OH)CO_2]_2O$. The results are given in Table 1 which show an accuracy of about 1% as compared to the value obtained using volumetric method.

Effect of foreign ions — Interference due to Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, UO^{2+}, Cr^{3+}, Ti^{4+} Ce^{4+}, Cl^-, NO_2^-, NO_3^-, SO_4^{2-} and CrO^{-4}_{2} was studied. Ti^{4+}, Cr^{2+}, Cl^- and SO_4^{2-} do not interfere. The estimations which were carried out in the presence of varying amounts of foreign ions indicate that for each 100 mg of manganese solution, the tolerance limit is 10 mg for all the divalent cations (except UO_2^{2+}) whereas only 5 mg of Ce^{4+} and UO_2^{2+} are tolerated. The anions NO_2^-, NO_3^- and CrO_4^{2-} interfere seriously since these anions oxidize benzilate and should be avoided under the condition of the experiment.

Estimation of Mn(II) in pyrolusite — The mineral was first dissolved in hydrochloric acid and contaminated Fe(III) removed by complexing the latte with ammonium bifluoride. After adjusting the *p*H, between 3·2 and 5·4 sodium benzilate solution was added. The precipitate was then washed, filtered, dried and weighed to constant weight. The accuracy of the method was found to be ± 1% as compared to the value obtained by volumetric method using bismuthate (Table 1).

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Determination of V(V) & Cr(VI) in Presence of Chloride

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Received 10 *November* 1975; *accepted* 24 *May* 1976

Two methods are described for the titrimetric estimation of V(V) and Cr(VI) in the presence of chloride. They differ only in the manner in which preferential oxidation of V(IV) by potassium permanganate is carried out. In the first method two titrations are recommended at room temperature in order to provide requisite time for V(IV) oxidation. The second method is useful when simultaneous estimation is to be done in the same aliquot. Here the solution is cooled to 5° and then V(IV) is oxidized selectively with excess potassium permanganate. Oxidation of Cr(III) which becomes prominent in the presence of chloride is made negligible in these methods.

AMONGST the titrimetric methods for the estimation of vanadium(V) and chromium(VI), the one generally employed involves titration with standard iron(II) sulphate in sulphuric acid medium in the presence of phosphoric acid, using diphenylamine sulphonate as the indicator[1,2]. This gives the total titre value for both V(V) and Cr(VI). The vanadium is then selectively oxidized with excess potassium permanganate and after destroying the latter, V(V) is retitrated with iron(II); Cr(III) remains unaffected and its value is obtained by difference[3]. During our work on the recovery of

TABLE 1 — INFLUENCE OF CHLORIDE

[Vanadium and chromium in each experiment, 10·12 and 3·47 mg respectively; time for V(IV) oxidation 3 min; temp. 28°]

NaCl added mg	Vanadium found mg	NaCl added mg	Vanadium found mg
10	10·12	100	10·19
25	10·16	250	10·29
50	10·19	500	10·40

vanadium from bauxite residues (which also contain chromium) we found that conventional method of vanadium-chromium analysis in a mixture is subject to inaccuracies when chloride is present in the system. The present note reports two simple modified procedures for the estimation of V(V) and Cr(VI) in the presence of chloride.

The oxidation of vanadium(IV) by permanganate is a sluggish reaction necessitating addition of excess oxidant to ensure complete conversion to V(V). Chromium(III) can also be oxidized by permanganate in acid solution but the reaction can be made negligible when oxidizing V(IV)-Cr(III) mixtures by controlling the excess permanganate and time. The sluggish reaction of V(IV) with permanganate can be made to proceed rapidly at an elevated temperature but then Cr(III) gets increasingly oxidized. Presence of chloride further complicates the selective oxidation of V(IV), giving higher values of V(V) (Table 1) in vanadium-chromium analysis. We have observed that at room temperature (25-30°) oxidation of Cr(III) is negligible in 2 min but becomes significant as the time is increased. If sodium chloride is present concurrently, Cr(III) oxidation even in the short period of 2 min is not negligible and increases with increasing time. Oxidation study at different temperatures revealed that Cr(III) oxidation in the presence or absence of chloride decreases with decrease in temperature and becomes negligible at 5° or below without affecting the complete oxidation of V(IV). Even when excess permanganate is kept for 10 min at 5°, Cr(III) is not oxidized, thereby affording a simple method for the estimation of vanadium in the presence of both chloride and Cr(III) (Procedure B).

If it is preferred to oxidize V(IV) selectively in the presence of Cr(III) and chloride at room temperature, permanganate is to be added dropwise till it is in slight excess as indicated by its pink colour. In the presence of diphenylamine sulphonate indicator this may be difficult due to intense colour of the indicator. For the analysis of vanadium-chromium mixture in the presence of chloride therefore two titrations are recommended (Procedure A). Both the procedures gave similar results and any one could be adopted.

Reagent grade chemicals were used. Solutions (0·02*N*) of potassium dichromate, sodium vanadate, and ammonium ferrous sulphate were prepared in distilled water. The solutions of other reagents were potassium permanganate (0·1*N*), sulphamic acid (10%), sodium nitrite (0·5%) and barium diphenylamamine sulphonate indicator (0·2%).

TABLE 2 — DETERMINATION OF VANADIUM AND CHROMIUM IN PRESENCE OF CHLORIDE

(Sodium chloride added in each case 500 mg)

Vanadium, mg			Chromium, mg		
Taken	Found	Diff.	Taken	Found	Diff.
		PROCEDURE A			
1·00	1·00	0·00	20·00	20·09	0·09
5·00	5·00	0·00	15·00	15·10	0·10
10·00	10·06	0·06	10·00	9·95	0·05
15·00	15·10	0·10	5·00	4·95	0·05
20·00	20·01	0·01	1·00	1·00	0·00
		PROCEDURE B			
1·00	1·00	0·00	20·00	20·10	0·10
5·00	5·02	0·02	15·00	15·20	0·20
10·00	10·00	0·00	10·00	10·08	0·08
15·00	15·10	0·10	1·00	1·00	0·00

Procedure A — To an aliquot (of a mixture) containing dichromate, vanadate and sodium chloride, sufficient 1 : 1 sulphuric acid to maintain an overall acidity of 2*N* and 5 ml syrupy phosphoric acid were added. The solution was diluted to 100 ml and the mixture titrated with standard iron(II) solution after adding 2-3 drops of indicator solution. The titre value corresponds to the sum of vanadium(V) and chromium(VI) present in the mixture. To another similar aliquot of a mixture under similar conditions calculated (corresponding to the titre value above) quantity or little excess of iron(II) solution was added, followed by dropwise addition of permanganate with constant stirring (preferably magnetic) till its colour persisted for 2 min. Excess permanganate was reduced by adding just sufficient sodium nitrite solution and excess of the latter was destroyed with 10 ml of sulphamic acid. The vanadate formed was titrated with iron(II) solution after adding 2-3 drops of indicator solution. The chromium value was obtained by difference.

Procedure B — The total vanadium and chromium in an aliquot was estimated by iron(II) titration as in procedure A. After the end point had reached the solution was cooled to 5°. An excess of permanganate solution was added with constant stirring (preferably magnetic) for 3 min. Thereafter permanganate was destroyed by sodium nitrite and sulphamic acid as before. The solution was now brought to room temperature (25-30°) and the vanadate formed titrated with iron(II) solution. The chromium value was obtained by difference.

Representative data of a series of experiments are given in Table 2.

The authors thank Prof. P. K. Jena, Director, for his keen interest in the work.

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