
**COULOMETRIC DETERMINATION OF HYDROQUINONE,
4-AMINOPHENOL AND METHOL
WITH TRIVALENT MANGANESE FLUORIDE COMPLEX***

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The possibility of the coulometric generation of trivalent manganese in fluoride solutions was examined and the current efficiency was measured in dependence on the solution composition and current density. Direct coulometric titrations of reversibly oxidizable organic compounds were tested on hydroquinone, 4-aminophenol, and methol in milligram and microgram quantities. As a more convenient approach, a method of coulometric retitration of trivalent manganese fluoride complex with divalent iron was worked out and its limits were established. The applicability of the trivalent manganese-divalent iron dual system to the indirect determination of the above model organic substances was verified.

The preparation, properties, and analytical use of complexes of trivalent manganese have been reviewed previously^{1,2}; the possibility of the analytical application of the coulometric generation of trivalent manganese compounds has been discussed in the review³. Solutions of the fluoride complex of trivalent manganese prepared chemically⁴ have been used for the titrimetric determination of hydroquinone, 4-aminophenol, and methol⁵ as well as for their indirect spectrophotometric determination⁶.

In fluoride solutions, trivalent manganese can be generated⁷ with a 100% current efficiency using manganese(II) sulphate, sulphuric acid, and potassium fluoride, each in a concentration of 0.5 mol l^{-1} , as the base electrolyte and applying a current density of 10 mA cm^{-2} . Up to now, however, the dependence of the current efficiency on the composition of the generating solution, *i.e.*, the concentrations of the three components, or on the current density has not been examined.

Coulometrically generated trivalent manganese in fluoride solutions has been used for the determination of divalent iron⁸ and tetravalent uranium⁹; organic substances, however, have not been so far analyzed in this fashion. The present work deals with the use of coulometrically generated trivalent manganese in this system for the determination of some organic substances. It is an advantage of this

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approach that lower acidities can be applied, whereupon the reactivity and consequently the rate of adverse consecutive reactions are lowered and the stability of the reagent is improved; this is of particular importance for indirect determinations. Also, the formal redox potential of the Fe(II)/Fe(III) system is lowered appreciably in the presence of fluoride, which is associated with a higher and steeper potential jump for the retitration of trivalent manganese with divalent iron.

EXPERIMENTAL

Reagents and Apparatus

Volumetric solutions of hydroquinone, 4-aminophenol, and methol (5 mmol l^{-1}) were prepared by dissolving the solid chemicals in 500 ml of 0.5M sulphuric acid and diluting to 1 litre with distilled water. Solutions ten times more dilute were obtained by diluting the stock solutions with water, and their titre was determined in 24 h with potassium dichromate¹⁰. Volumetric solutions of iron(II) sulphate (50, 10 and 1 mmol l^{-1}) in 0.5M sulphuric acid, potassium dichromate (0.1/6, 0.01/6 and $0.001/6 \text{ mol l}^{-1}$) in distilled water, cerium(IV) sulphate (10 and 1 mmol l^{-1}) in 1M sulphuric acid, and potassium permanganate (10 mmol l^{-1}) in distilled water were prepared and standardized conventionally¹¹. Solution of iron(III) sulphate (0.5 mol l^{-1}) was obtained by long-run (2–4 days) dissolution of the solid chemical in 1 litre of 1M sulphuric acid and filtration over an S4 frit. All the chemicals used were of reagent grade purity.

The coulometric measurements were performed on an OH 404 automatic coulometric analyzer (Radelkis, Budapest). A 200 ml polyethylene vessel was used in which the anode and cathode compartments were separated by a frit with agar-agar. A platinum sheet of 2 cm^2 surface area served as the generating electrode and a coiled platinum wire as the auxiliary electrode. The potentiometric measurements were carried out with a GTE digital transistor pH-meter (Seibold, Vienna) using a bright platinum indicator electrode and a saturated calomel reference electrode. The solution was delivered from a 10 ml burette with 0.02 ml divisions adapted so that the volume of a drop from the burette was 0.02 ml.

Procedures

Study of the current efficiency. Using 100 ml of base solution of a chosen composition, the time of generation of trivalent manganese was varied in dependence on the generating current so that the consumption of the iron(II) sulphate volumetric solution in the retitration was between 5 and 10 ml. The concentrations of iron(II) sulphate were 1, 10, and 50 mmol l^{-1} for currents of 1–5 mA, 10–50 mA, and 100 mA, respectively. The procedure for the study of the current efficiency of generation of divalent iron was similar; cerium(IV) sulphate (10 mmol l^{-1}) was used for the retitration. The current efficiency was calculated as the ratio of the experimental to the theoretical consumptions.

Direct coulometric titration of hydroquinone, 4-aminophenol and methol. To 100 ml of base solution of a chosen composition was added 10.00 ml of solution containing 2–8 mg of hydroquinone or 4-aminophenol or 4–15 mg of methol, and a coulometric titration with potentiometric indication was carried out. For hydroquinone the base solution contained manganese(II) sulphate, sulphuric acid, and potassium fluoride in concentrations of 0.5, 0.5, and 0.4 mol l^{-1} , respectively, and a generating current of 20 mA corresponding to the current density of $10 \text{ mA} \cdot \text{cm}^{-2}$ was used. On a semimicro scale, 200–800 μg of hydroquinone was taken and a gener-

ating current of 2 mA, corresponding to the current density of 1 mA cm^{-2} , was used. For 4-aminophenol and methol, the generating solution contained manganese(II) sulphate, sulphuric acid, and potassium fluoride in concentrations of 0.5, 1, and 0.5 mol l^{-1} , respectively, the 15 mA generating current corresponded to a current density of 7.5 mA cm^{-2} .

Coulometry using the trivalent manganese-divalent iron dual system. The base electrolyte was pretreated as follows. To determine oxidizable impurities (divalent iron in particular), 20.00 ml of iron(III) sulphate (0.5 mol l^{-1}) solution in 1M sulphuric acid used for the preparation of the generating solution was titrated potentiometrically with cerium(IV) sulphate titrant solution (10 mmol l^{-1}). The base solution then was made up by mixing 500 ml of manganese(II) sulphate (1 mol l^{-1}), 100 ml of sulphuric acid (5 mol l^{-1}), 100 ml of potassium fluoride (4 mol l^{-1}), and 200 ml of iron(III) sulphate (0.5 mol l^{-1}) solutions. To this system was added solution of potassium permanganate (10 mmol l^{-1}) in a volume about 20% exceeding that required for the oxidation of the impurities found, and the whole was diluted to 1 litre and stored in a polyethylene bottle. After oxidizing the impurities present, the permanganate added reacted with divalent manganese to give trivalent manganese fluoride complex. Prior to each experiment, 100 ml of this generating solution was added to the generating vessel and the trivalent manganese fluoride complex was titrated coulometrically with divalent iron precisely to the equivalence point. Only then the solution was used for the measurements.

Indirect coulometric determination of hydroquinone, 4-aminophenol and methol. For a current density of 5 mA cm^{-2} , 100.0 ml of the generating solution modified as above is taken and trivalent manganese is generated in it so that the charge passed is about 20 C. 10.00 ml of solution containing 2–8 mg of hydroquinone or 4-aminophenol or 4–14 mg of methol is added, the system is stirred thoroughly and in 5 min, the unreacted trivalent manganese fluoride complex is coulometrically titrated with divalent iron using potentiometric indication. The weight of the substance determined, in mg, is calculated as $m = k(A - B)$, where A and B are the charges, in coulombs, required for the generation of trivalent manganese and divalent iron, respectively, and the constant k is 0.5706 for hydroquinone, 0.5655 for 4-aminophenol, and 0.8926 for methol.

For a current density of 1 mA cm^{-2} the procedure is analogous, only the amount of trivalent manganese generated should correspond to a charge of about 2 C and the 10.00 ml of solution should contain 250–800 μg of hydroquinone or 4-aminophenol or 400–1 400 μg of methol.

RESULTS AND DISCUSSION

Direct Coulometric Titrations

The rate of oxidation of organic substances by trivalent manganese is known^{1,2} to depend appreciably on acidity and on the concentration of the complexing substance. The dependence of the current efficiency on the potassium fluoride and sulphuric acid concentrations was therefore examined and the dependence of the current efficiency on the current density was then measured in optimum conditions. The results obtained were used to suggest the optimum conditions for the direct coulometric titration of hydroquinone, 4-aminophenol, and methol.

The dependence of the current efficiency of generation of the trivalent manganese fluoride complex on the concentration of potassium fluoride was measured in solutions with $c_{\text{H}_2\text{SO}_4} = 1, 0.5, \text{ and } 0.4 \text{ mol l}^{-1}$. The concentration of manganese(II)

sulphate was held at 0.5 mol l^{-1} because at lower concentrations hydrated manganese dioxide separates on the generating electrode, particularly at higher current densities. The data obtained are given in Table I, each result being the average of triplicate measurements. The fact that the observed current efficiency decreases with decreasing concentration of potassium fluoride can be explained in terms of tetravalent manganese formation in solutions with lower concentrations of the complexant. The decrease in the current efficiency occurring if the concentration of potassium fluoride is raised above 0.5 mol l^{-1} may be associated with the hydrolysis of divalent manganese in solutions with higher pH, the sulphuric acid present being partly neutralized by the fluoride; this is borne out by the considerable current efficiency drop in systems with $c_{\text{H}_2\text{SO}_4} = 0.4 \text{ mol l}^{-1}$, $c_{\text{KF}} = 0.5 \text{ mol l}^{-1}$, accompanied by a visible separation of hydrated manganese(II) oxide. The possibility of using solutions with low acidities and high potassium fluoride concentrations is thus limited by the hydrolysis of divalent manganese.

The potentiometric titration curves obtained are shown in Fig. 1. Under otherwise constant conditions, the formal redox potential of the Mn(III)/Mn(II) system increases with increasing concentration of potassium fluoride. In all cases, however, the potential change in the equivalence point was rapid, high, and steep enough. For instance, in a system with $c_{\text{MnSO}_4} = c_{\text{H}_2\text{SO}_4} = 0.5 \text{ mol l}^{-1}$, $c_{\text{KF}} = 0.4 \text{ mol l}^{-1}$, this potential change was about 25 mV per 0.02 ml of iron(II) sulphate solution (0.01 mol l^{-1}) and the potential established within 60 s.

TABLE I

Dependence of the current efficiency of generation of trivalent manganese fluoride complex on the concentrations of potassium fluoride and sulphuric acid. Manganese(II) sulphate concentration 0.5 mol l^{-1} , current density 10 mA cm^{-2}

c_{KF} mol l^{-1}	Current efficiency, %, for $c_{\text{H}_2\text{SO}_4}$ (mol l^{-1})		
	1	0.5	0.4
0.1	90.65	91.52	84.72 ^a
0.2	94.20	94.02	97.32
0.3	95.56	99.05	98.56
0.4	96.60	100.22	98.15
0.5	99.75	99.12	59 ^b

^a Hydrated manganese(IV) oxide separates on generating electrode; ^b white precipitate of hydrated manganese(II) oxide separated from the generating solution in a time.

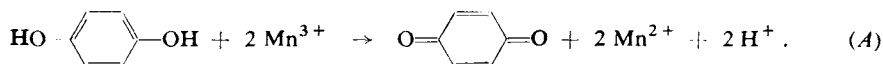
It can be thus concluded that the titration of the fluoride complex of trivalent manganese with iron(II) sulphate can be applied also to the determination of the unreacted excess of coulometrically generated reagent in indirect determinations.

The dependence of current efficiency on current density was measured in solutions with $c_{\text{MnSO}_4} = c_{\text{H}_2\text{SO}_4} = 0.5 \text{ mol l}^{-1}$, $c_{\text{KF}} = 0.4 \text{ mol l}^{-1}$. The data obtained are as follows:

Current density, mA cm^{-2}	1	2	5	10	15	20	50
Current efficiency, %	100.12	100.06	99.98	100.04	97.03	94.95	93.48

The decrease in the current efficiency at higher current densities can again be explained in terms of the formation of hydrated manganese(IV) oxide on the generating electrode surface.

The potential change in the direct coulometric titration of hydroquinone, at a current density of 10 mA cm^{-2} , was about 60 mV per 50 mC. The potential established within 5 min, so that the complete titration took as much as 40 min. According to the charge passed, 1 mol of hydroquinone reacts with 2 mol of trivalent manganese fluoride complex, which is consistent with equation (A),



The titration curves are shown in Fig. 2.

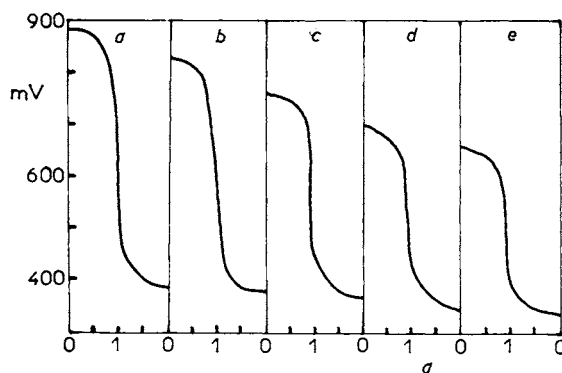
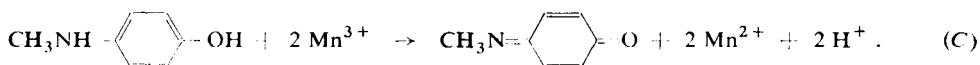
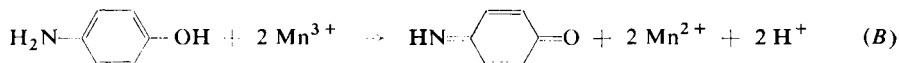


FIG. 1

Potentiometric titration of trivalent manganese fluoride complex with iron(II) sulphate (10 mmol l^{-1}); $c_{\text{H}_2\text{SO}_4} = c_{\text{MnSO}_4} = 0.5 \text{ mol l}^{-1}$, $c_{\text{KF}} (\text{mol l}^{-1})$: a 0.1, b 0.2, c 0.3, d 0.4, e 0.5. a — degree of titration

For 4-aminophenol and methol, optimum results were obtained in solution with $c_{\text{MnSO}_4} = c_{\text{KF}} = 0.5 \text{ mol l}^{-1}$, $c_{\text{H}_2\text{SO}_4} = 1 \text{ mol l}^{-1}$ at a current density of $7.5 \text{ mA} \cdot \text{cm}^{-2}$ (ref.¹²). The consumption of reagent again corresponded to a two-electron oxidation of analyte according to equations (B) and (C),



The potential change in the equivalence point region was about 30 mV per 50 mC. The potential established more slowly than with hydroquinone, which precluded application of this procedure on a micro scale.

The accuracy and reproducibility of the direct coulometric titration of the three substances are documented by Table II.

Coulometry with the Trivalent Manganese-Divalent Iron Dual System

In view of the slowly establishing potentials in the direct coulometric titrations of the substances under study, attention was paid to the indirect approach using the trivalent manganese-divalent iron dual system. Here the requisite amount of trivalent manganese is generated in a base solution containing divalent manganese and trivalent iron, the trivalent manganese is allowed to react with analyte, and

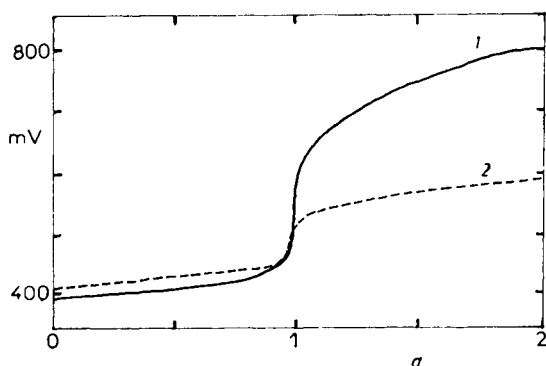


FIG. 2

Potentiometric titration curves for the direct coulometric titration of hydroquinone with trivalent manganese fluoride complex; $c_{\text{MnSO}_4} = c_{\text{H}_2\text{SO}_4} = 0.5 \text{ mol l}^{-1}$, $c_{\text{KF}} = 0.4 \text{ mol l}^{-1}$. Current density (mA cm^{-2}): 1 10, 2 1. a — degree of titration

the unreacted excess is determined coulometrically with divalent iron on inverting the generating electrode polarity.

Divalent iron can be generated with a 100% current efficiency from acid solutions of iron(III) sulphate¹³, or in complexing solutions¹⁴. Therefore, it was first sought whether the presence of divalent manganese or potassium fluoride leaves the current efficiency of divalent iron generation unaffected. The experiments were performed in solutions with $c_{\text{MnSO}_4} = c_{\text{H}_2\text{SO}_4} = 0.5 \text{ mol l}^{-1}$, $c_{\text{KF}} = 0.4 \text{ mol l}^{-1}$,

TABLE II

Accuracy and reproducibility of direct coulometric titration of hydroquinone, 4-aminophenol and methol with trivalent manganese fluoride complex

Prepared mg	Found ^a mg	Standard deviation mg
Hydroquinone ^b		
2.727	2.735	0.009
5.453	5.474	0.010
8.175	8.188	0.009
Hydroquinone ^c		
0.278	0.276	0.002
0.555	0.553	0.003
0.833	0.828	0.001
4-Aminophenol ^d		
2.734	2.774	0.015
5.469	5.520	0.032
8.203	8.315	0.044
Methol ^d		
4.659	4.690	0.024
9.318	9.409	0.031
13.976	14.175	0.082

^a Average of 7 replicate determinations from which the standard deviation was also calculated; ^b $c_{\text{MnSO}_4} = c_{\text{H}_2\text{SO}_4} = 0.5 \text{ mol l}^{-1}$, $c_{\text{KF}} = 0.4 \text{ mol l}^{-1}$, current density 10 mA cm^{-2} ; ^c current density 1 mA cm^{-2} ; ^d $c_{\text{MnSO}_4} = c_{\text{KF}} = 0.5 \text{ mol l}^{-1}$, $c_{\text{H}_2\text{SO}_4} = 1 \text{ mol l}^{-1}$ current density 7.5 mA cm^{-2} .

$c_{\text{Fe}_2(\text{SO}_4)_3} = 0.1 \text{ mol l}^{-1}$. (This composition was adhered to in all the subsequent experiments.) The following current efficiencies of divalent iron generation were obtained:

Current density, mA cm^{-2}	1	2	5	10
Current efficiency, %	99.94	100.21	100.14	99.89

Higher current densities were not used because the current efficiency of generation of trivalent manganese fluoride complex does not reach 100% with them.

Furthermore, it was sought whether the presence of trivalent iron affects the current density region over which the trivalent manganese generation takes place with a 100% current efficiency. The dependence of the current efficiency of trivalent manganese generation on the current density was examined in solutions as above, and the following data were obtained:

Current density, mA cm^{-2}	1	2	5	10
Current efficiency, %	100.21	100.14	99.82	90.42

Finally, the applicability of the coulometric method using the trivalent manganese–divalent iron was tested with respect to the equality of the charge required for the retitration of trivalent manganese with divalent iron and the charge used up for the generation of the trivalent manganese. In solutions as above, the following ratios of the charges for the generation of equivalent amounts of trivalent manganese and divalent iron were obtained:

Current density, mA cm^{-2}	1	2.5	5	7.5	10
Charge ratio	1.0048	1.0063	1.0012	1.1042	1.1138

Thus, the charge ratio is virtually unity up to the current density 5 mA cm^{-2} . The increase in this ratio at higher current densities can be explained by the decreasing current efficiency of generation of trivalent manganese in the presence of trivalent iron.

The potentiometric titration curve for the coulometric retitration of trivalent manganese fluoride complex generated by divalent iron, for a current density of 5 mA cm^{-2} , is shown in Fig. 3. The potential establishes rapidly enough even in the equivalence point range and its change in this range is approximately 100 mV per 50 mC at a current density of 5 mA cm^{-2} .

Over the time period examined, the ratio of the charges requisite for the generation of equivalent amounts of trivalent manganese and divalent iron at a current density of 5 mA cm^{-2} remains unity regardless of the time in which the retitration is carried out. Hence, no appreciable loss of trivalent manganese occurs within 60 min. Longer

TABLE III

Time course of oxidation of hydroquinone, 4-aminophenol and methol with trivalent manganese fluoride complex (10.00 ml of solution)

Concentration mmol l ⁻¹	Consumption of reagent mol/l in time, min				
	2	5	10	30	60
Hydroquinone					
5	2.000	2.000	2.005	2.028	2.040
0.5	2.001	1.995	2.004	2.020	2.040
4-Aminophenol					
5	2.002	1.998	2.010	1.998	2.040
0.5	1.980	1.996	2.024	2.045	2.050
Methol					
5	2.008	2.011	2.021	2.050	2.228
0.5	1.996	2.002	1.999	2.047	2.108

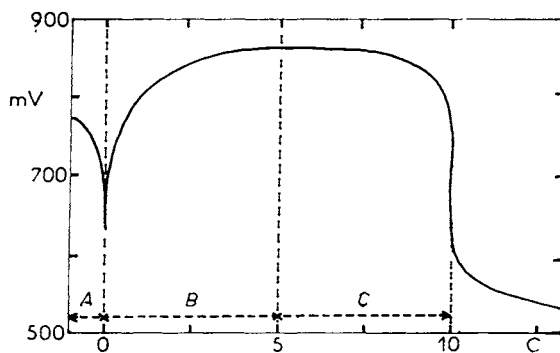


FIG. 3

Potentiometric indication of coulometric generation of trivalent manganese and its retitration with divalent iron. Regions: *A* generation of iron(II) for the reduction of manganese(III) emerged from excess permanganate during the generating solution pretreatment; *B* generation of manganese(III); *C* generation of iron(II) for the retitration of trivalent manganese fluoride complex

times were not pursued because for reactions proceeding more slowly, a more reactive form of trivalent manganese, such as manganese(III) sulphate, would be preferred.

Indirect Coulometric Determination of Hydroquinone, 4-Aminophenol and Methol

The data of the time course of the oxidation are given in Table III. Each value is the average of triplicate measurements which did not differ more than $\pm 0.2\%$.

TABLE IV

Accuracy and reproducibility of indirect coulometric determination of hydroquinone, 4-aminophenol and methol

Current density mA cm^{-2}	Prepared mg	Found ^a mg	Relative standard deviation %
Hydroquinone			
5	2.704	2.705	0.55
5	5.408	5.583	0.50
5	7.446	7.430	0.47
1	0.277	0.278	0.65
1	0.555	0.556	0.40
1	0.832	0.832	0.56
4-Aminophenol			
5	2.747	2.753	0.44
5	5.401	5.385	0.44
5	8.102	8.109	0.32
1	0.279	0.276	0.97
1	0.557	0.560	0.77
1	0.835	0.840	0.66
Methol			
5	4.658	4.674	0.14
5	9.315	9.313	0.05
5	13.977	14.028	0.09
1	0.486	0.489	0.86
1	0.972	0.975	0.76
1	1.458	1.452	0.80

^a Average of seven replicate determinations from which the standard deviation was also calculated.

The oxidation is quantitative on a 2 min action of excess reagent, and a slightly deeper oxidation of analyte only takes place if the action time is extended to an hour. The accuracy and reproducibility of determination according to the procedure suggested are documented by Table IV.

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