

**A NEW METHOD FOR SYNTHESIS OF MANGANESE(III)  
ACETATE DIHYDRATE**

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**ABSTRACT**

A new method is reported for the synthesis of manganese(III) acetate dihydrate from manganese(II) acetate tetrahydrate, lead(IV) oxide and acetic acid as solvent. Melting point, mixed melting point with manganese(III) acetate dihydrate obtained by the well - known Christensen method, elemental analyses, and potentiometric titration with a standard hydroquinone solution in acetic acid showed that the compound obtained by the new method was very pure (99.6%). In addition a solution of the compound in acetic acid was used to titrate potentiometrically some hydrazine derivatives and excellent results were obtained.

**INTRODUCTION**

Manganese(III) acetate dihydrate is potentially of importance because of its diverse possible uses in chemical reactions, (1) the synthesis of coordination compounds of manganese(III) ion<sup>1-5</sup>, (2) in organic synthesis as a specific oxidizing agent<sup>6-10</sup>, (3) and in redoximetric titrations of some organic compounds<sup>11-14</sup>.

However up to now the uses of manganese(III) acetate have remained limited. This is probably due to the time consuming synthetic methods required for its production<sup>15-22</sup>.

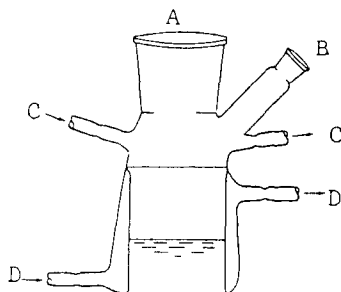


Figure 1. Cell designed for potentiometric titrations. The cell is equipped with a combined platinum and Ag-AgCl electrodes through A, and with curved thin-tip semimicro burette through B, nitrogen through C, and constant temperature water through D.

We now describe a method with the following advantages over the older methods; (1) the purity and the yield of the compound obtained by this method are very high, (2) the starting materials are inexpensive and readily available.

## EXPERIMENTAL

### Apparatus

A chemtrix 60A pH meter equipped with a combined platinum electrode and a modified Ag-AgCl electrode assembly was used for the potentiometric titrations. The Ag-AgCl was modified by emptying its aqueous KCl solution and refilling it with a saturated solution of KCl in dry methanol. Titrations were carried out in a specially designed cell which is illustrated in fig 1. The cell connected to a water-circulating thermostat which kept the temperature of the cell and its content at  $20 \pm 1^\circ\text{C}$ .

### Chemicals

Lead(IV) oxide: Purchased from Fluka, 99 % in purity, and was used as purchased.

Manganese(II) acetate tetrahydrate: Purchased from Merck, 99 % in purity, and was used without further purification.

Acetic acid: Purchased from Merck, 99 - 100 % in purity, and was purified by fractional distillation over chromic acid.

Hydroquinone: Purchased from Riedel de Haen, 99.8 % in purity, and was used after recrystallization from dry ethanol.

4-Nitrophenylhydrazine: Purchased from Merck, 98 % in purity, and was used after purification from dry ethanol.

Diphenylcarbazine: Purchased from Merck (pure) and was used after recrystallization from dry ethanol.

Semicarbazide hydrochloride: Purchased from Merck, 99.8 % in purity, and used after recrystallization from dry ethanol.

### Synthesis of Manganese(III) Acetate Dihydrate

Manganese(II) acetate tetrahydrate (7.35 g, 0.030 mol) and lead(IV) oxide (2.39 g, 0.010 mol) in a 150 mL flask were treated with acetic acid (75 mL) and the stirred mixture heated to 50-60°C until the black lead(IV) oxide dissolved. The resulting dark brown solution was left overnight and the dark red coloured crystals formed were filtered off the suction using a coarse texture sintered glass crucible. The crystals were washed twice with 10 mL portions of dry acetic acid, and recrystallised from 50 mL of dry acetic acid. The resulting dark red needles were washed with two 5 mL portions of dry acetic acid and dried in a vacuum oven at 30°C, yield 90 % based on  $\text{PbO}_2$ , mp 115°C (decomp), calc. for  $\text{C}_6\text{H}_{13}\text{O}_8 \text{Mn}$ , C 26.88, H 4.8 % ; found: C 26.83, H 4.85 %.

The purity of the product was further tested as follows. A standard hydroquinone solution of 0.02998 M was prepared from

Table 1. Purity Testing of Manganese(III) Acetate Dihydrate Titrations with Standard Hydroquinone Solution.

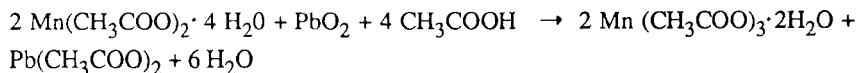
Taken (mg)	Found (mg)	Purity (%)
5.41	5.39	99.6
3.90	3.86	99.0
7.00	6.99	99.9
4.19	4.18	99.8
7.48	7.47	99.9

Mean value :  $99.6 \pm 0.4$  % manganese(III) acetate

analytically pure hydroquinone. Solutions of known masses of Mn (III) acetate dihydrate were titrated potentiometrically against the hydroquinone solution. Results are given in Table 1.

## RESULTS AND DISCUSSION

A new method is described for the synthesis of manganese(III) acetate dihydrate from manganese(II) acetate tetrahydrate, lead(IV) oxide and acetic acid as solvent.



When  $\text{PbO}_2$  (1 mol) is treated with an excess of Mn(II) acetate (3 mol) in HOAc the Pb(IV) oxide reacts quantitatively producing Mn(III) acetate (isolated by crystallization) and a solution containing Pb(II) acetate and the excess of Mn(II) acetate. Traces of the latter

salts are easily removed from the Mn(III) acetate by washing with HOAc. The Mn(III) acetate is easily recrystallised from HOAc and the product is stable in a dark coloured bottle for several months at room temperature. The manganese(III) acetate dihydrate obtained by this method was tested for purity and was found to be sufficiently pure ( $99,6 \pm 0,4 \%$ ) to use in analytical procedures.

Similar titrations were conducted with the manganese(III) acetate dihydrate obtained by the Christensen method<sup>15</sup>, and the purity of the compound was found to be  $98,0 \pm 0,4 \%$ .

A 0.0150 M solution of manganese(III) acetate dihydrate in acetic acid was used in the titrations of hydrazine derivatives such as diphenylcarbazide, 4-nitrophenylhydrazine, and semicarbazide hydrochloride; we obtained excellent titration curves.

### CONCLUSIONS

The new method gives manganese(III) acetate dihydrate of  $99,6 \pm 0,4 \%$  purity and a yield based on Pb(IV) oxide of about 90 %.

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