Manganese

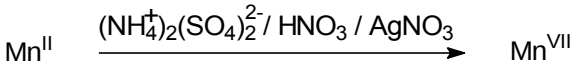
1. Determination of Manganese in Water

You have to determine the amount of manganese II in water. For this purpose, prepare a standard calibration curve with potassium permanganate. The aqueous manganese II salt solution is oxidized with ammonium peroxo disulfate, nitric acid and silver nitrate to give the Manganese VII salt (see reaction 1). The given water sample is measured three times.

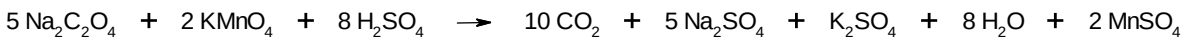
The potassium permanganate solution, facing the fact of its ever changing concentration, is titrated with the primary standard (see reaction 2) and the exact substance amount concentration *c*($KMnO_4$) is calculated.

2. Reaction Schemes:

Reaction 1



Reaction 2



3. Reagents for the Manganese Analysis:

Reagent	Amount	Information	Safety advice
Ammoniumperoxodisulfate	15*g*	Oxidation agent	H: 272-302-315-319-335-334-317 P:280-305+351+338-302+352-304+341-342+311
Nitric acid 65%	9*2.000*mL*	Oxidation agent	H: 272-314 P: 220-280-305+351+338-310
Silver nitrate 0.1M	9*2.000*mL*	Catalyst	272-314-410 P: 273-280-301+330+331-305+351+338-309+310
Sample with Mn II salt	3*10.00*mL*		H: 373-411 P: 273-314
di-Sodium oxlate	3*100*mg*	Primary standard	H: 302-312 P: 262

Potassium permanganate standard solution 0.02M	6.5mL calib. 3*15*mL*		H: 272-302-314-410 P: 220-273-280-305+351+338-310-501
Sulfuric acid about 20% in water	3*20*mL*	Acidifying agent	H: 314-290 P: 280-301+330+331-309-310-305+351+338

4. Equipment for Manganese Analysis

Analytical balance	1 4all	Wash bottle with water *nanopure*	1
Lab balance	1 4all	2.00*mL* volumetric pipet	2
Bin or flask with 2.5*L* water *nanopure*	1 4all	4.00*mL* volumetric pipet	2
Automatic burette with $KMnO_4$ 0.02*M*	1 4all	Beaker 400*mL*	1
Piston stroke pipette 1000*µL*	1 4all	100*mL* Erlenmeyer flask with stopper	3
Piston stroke pipette 2500*µL*	1 4all	Magnetic stirrer with heat plate	1
Beaker 100*mL*	4	Magnetic stirring bar	6
Volumetric flask 100*mL* with stopper	9	Magnetic Teflon stick	1
Marker pen	1	Thermometer (20-100°*C* must be visible)	1
Spatula	3	PS (Polystyrol) cuvettes	9
Funnel for transferring prepared solutions	2	Cuvette rack	1
10.00*mL* volumetric pipet	1	Measuring cylinder 25*mL*	1
250*mL* Erlenmeyer flask	1		

Pasteur pipettes as required.

5. Procedure:

Dissolved silver salts

Some of your volumetric flasks will contain silver nitrate salts. After use, they must be collected in special containers and never, under any circumstances, poured into the sink. They will be treated with sulfide later. (See number 13 *General Notes*)

Preparation of Ammonium Peroxo Disulfate Solution

Weigh out 15*g* Ammoniumperoxodisulfate in a 250*mL* Erlenmeyer flask, dilute it with not more than 50*mL* water *nanopure* and pour it quantitatively into a 100.0*mL* measuring flask. Then the flask is filled with water *nanopure* to the mark.

Preparation of the Samples

You have to prepare and measure the sample three times.

10.00*mL* of your sample are transferred by means of a volumetric pipet into a 100*mL* Erlenmeyer flask and diluted with approximately 10*mL* water. With a volumetric pipet transfer 2.00*mL* nitric acid $w(HNO_3) = 0.65 g/g$, 4.00*mL* of the previous prepared ammonium peroxo disulfate solution. Then add 2'000*µL* silver nitrate $c(AgNO_3) = 0.1 mol/L$ with a 2'500*µL* piston stroke pipet (Note 1). Heat the solution up to at least 75°*C* (Note 2). The Erlenmeyer flask is stoppered and under occasional stirring or swiveling the violet mixture is cooled down to ambient temperature during circa 90 minutes. You can have all three Erlenmeyer flasks on the same stirrer plate for cooling. The cool solution is then transferred quantitatively and without the magnetic stirring bar into a 100*mL* volumetric flask. All volumetric flasks are filled with water *nanopure* to the mark (Note 3) and well homogenized.

Preparation of Calibration Curve

Add 400*µL*, 850*µL*, 1'300*µL*, 1'750*µL* and 2'200*µL* of potassium permanganate $c(KMnO4) \approx 0.02 mol/L$ into 100.0*mL* volumetric flasks, which are reasonably marked. Into each flask, transfer with a volumetric pipet 2.00*mL* nitric acid $w(HNO_3) = 0.65 g/g$, 4.00*mL* of the previous prepared ammonium peroxo disulfate solution; Then add 2'000*µL* silver nitrate $c(AgNO_3) = 0.1 mol/L$ with a 2'500*µL* piston stroke pipet. All volumetric flasks are filled with water *nanopure* to the mark and well homogenized.

Blank solution

Transfer with a volumetric pipet 2.00*mL* nitric acid $w(HNO_3) = 0.65 g/g$, 4.00*mL* of the previous prepared ammonium peroxo disulfate solution into a 100*mL* volumetric flask. Then add 2'000*µL* silver nitrate $c(AgNO_3) = 0.1 mol/L$ with a 2'500*µL* piston stroke pipet. The volumetric flask is filled with water *nanopure* to the mark and well homogenized.

Photometry and Results

After homogenizing the absorbances are measured photometrically at 526*nm* against the blank solution. The photospectrometer is already prepared for measuring at this wavelength. There is only one photospectrometer in the lab. In view of this fact, you have to prepare the PS cuvettes and measure the samples without delay, if it's your turn.

Note all absorbances found, as well as the appropriate concentration in a reasonable manner in your protocol.

Calculations

Calculate the mass concentration β(Mn) in your sample with the aid of your calibration curve. Involve the result of the volumetric analysis.

A linear equation could be helpful. Alternatively you can calculate the mass concentrations β(Mn) in your samples with one point calibrations using close absorbances of the calibration curve. Also, you can use a blank excel-sheet on a computer or calculate with the aid of a hand calculator and millimeter paper.

6. Volumetric Analysis of Potassium Permanganate

Potassium permanganate standard solution is known for the fact that it tends to change its concentration slightly but steadily. In order to measure the exact amount of potassium permanganate we measure the exact substance amount concentration $c(KMnO_4)$ with the aid of the primary standard di-sodium oxalate.

Weigh three times approximately 100*mg* di-natrium oxalate directly into a 100*mL* beaker. Note the exact amount of di-natrium oxalate primary standard. Add 20*mL* water *nanopure* and 20*mL* sulfuric acid 20%. Stir by means of a magnetic stirrer until a clear solution is present. This solution is then warmed on a hot magnetic stirring plate up to at least 50 to 80°*C* (Note 2).

The warm solution is titrated with the standard solution to the endpoint visible on the change from colorless to a slight pink color (Note 4).

Calculate the exact substance amount concentration of your standard solution.

7. Notes

Note 1: There are four 50 or 100*mL* beakers. You can fill them with the reagent solutions and use them for pipetting conveniently. Take potassium permanganate solution from the automatic burette. Never pour reagent solutions back into the storage bottle. Pour waste reagents in the silver waste or, if there is no silver present, under dilution with fresh water into the sink.

Note 2: There is no harm, if the mixture is heated up to a slight boiling. Avoid heavy boiling; you could bias your analysis if there is some splashing. If you use a thermometer, rinse it well with water *nanopure* into the solution.

Note 3: There is a 400*mL* beaker present. You can fill it with a suitable amount of water *nanopure*. This is handy for filling up volumetric flasks.

Note 4: At the beginning of the addition add 1 – 2*mL* $KMnO_4$ solution. Then you have to wait a little and the deep violet color will disappear. After that you can continue with adding.

Protocols

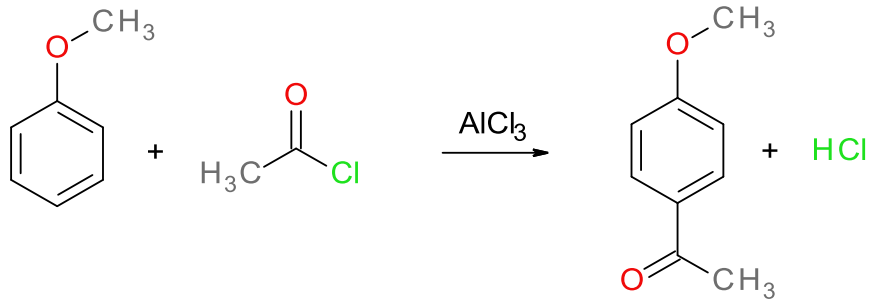
Write a protocol of the spectroscopic analysis on a blank sheet.
Write a protocol of your volumetric analysis on a blank sheet.
All found values must be noted clearly and in a reasonable order. Note your calculations in a reproducible way.

4-Methoxyacetophenone

8. Determination of 4-Methoxyacetophenone with External Standard on HPLC

A Friedel-Crafts reaction of anisole with acetyl chloride gives 4-methoxyacetophenone. In this case, an excess of anisole was used as solvent. The sample here is the raw product of 4-methoxyacetophenone with mainly anisole and a little tertiary butyl methyl ether from extraction as byproducts. It is your task to determine the amount of 4-methoxyacetophenone in the given sample.

9. Reaction Scheme of the Friedel-Crafts reaction



10. Reagents for HPLC Analysis

Reagent	Amount	Information	Safety advice
4-Methoxyacetophenone	ca. 2*50*mg*	Reference	H: 302-315 P: no advice
Raw 4-Methoxyacetophenone	ca. 2*100*mg*	Sample	*For Anisole:* H: 226 P: 210-262
Methanol HPLC grade	ca. 500*mL*	For dilution	H: 225-331-311-301-370 P: 210-233-280-302+352
Water nanopure HPLC grade	ca. 150*mL*	For dilution	No advice

11. Equipment for HPLC Analysis

Analytical balance	1 4all	Weighing tongs	1 4all
Volumetric flask with stopper 50*mL*	4	Piston stroke pipet 100*µL*	1 4all
Erlenmeyer flask with stopper 1000*mL*	1	Crimp capped sample vials	4
Measurement cylinder 250*mL*	1	Crimp cap tongs	1 4all
Spatula	2	Rack for vials	1
Piston stroke pipet 1000*µL*	1 4all		

Pasteur pipettes as required.

12. Procedure

Preparation of diluent

In a stoppered 500*mL* Erlenmeyer flask, 200*mL* methanol *for HPLC* and 200*mL* water *nanopure* (for HPLC) are mixed until a clear solution is present.

Dilution of the reference

Approximately 55*mg* 4-methoxyacetophenone are filled in a 50.0*mL* volumetric flask, weighed exactly and diluted with methanol / water nanopure 1:1 diluent to the mark. The solution is homogenized well. 625*µL* of the solution is pipetted with a 1000*µL* piston stroke pipette into a 25.0*mL* volumetric flask and diluted with methanol / water nanopure 1:1 diluent to the mark.
This procedure is done twice and the flasks are reasonably labelled.

Dilution of the sample

With the aid of a piston stroke pipet 100*µL* sample are dropped into a 50.0*mL* volumetric flask and the weigh is taken exactly. The sample is diluted with methanol / water nanopure 1:1 diluent to the mark. The solution is homogenized well. 625*µL* of the solution is pipetted with a 1000*µL* piston stroke pipette into a 25.0*mL* volumetric flask and diluted with methanol / water nanopure 1:1 diluent to the mark.
This procedure is done twice and the flasks are reasonably labelled.

Preparation of vials

From each diluted volumetric flask a sample is taken and filled into a crimp vial. The crimp vial is tightly capped and clearly marked with a marker pen with sample*1*, sample*2*, reference*1* and reference*2*. Then it is handed over to the HPLC operator. The chromatograms are taken by the HPLC operator with a prepared and tested method. You have to add them to the protocol as an appendix.

HPLC parameters

Stationary Phase:	NUCLEOSIL 120-5 C-18
Temperature:	35°*C*
Mobile phase:	methanol / water 65% / 35% with 0.7*mL*/*min* flow, 1.2*min* stop time.
Injection:	10*µL*
Detection:	278*nm*

4-Methoxyacetophenon will give a clear, symmetric peak at about 0.7*min* with a height of 300 to 500*mAU*. Anisole will give a small symmetric peak at about 0.9*min* with a small height.

Schedule for HPLC

One analysis run needs 2 minutes time from injection to injection. You have to hand over your samples before 2:30 p.m. for the HPLC analysis. Otherwise there might not be enough time for your samples to run.

Calculations

Calculate the percentage of 4-methoxyacetophenon in the sample with the method of external standard; Once with reference*1* and sample*1* and once with reference*2* and sample*2*.
Calculate the mean value of the two percentages.
Calculate the recovery with reference*1* as reference and reference*2* as a virtual sample. The found recovery percentage should be between 98 to 102%.

Protocols and calculations HPLC analysis

Your protocol must contain a suitable table with the amounts of your sample and those of your references. In this table, write down the found areas and the results of your calculations. Describe your dilution work in a few words.

The calculation work can be done on a separate blank sheet or on a excel sheet on a computer.

Note your calculations in a reproducible way.

13. General Notes

You must pour all solutions containing silver in a special bin labeled "Ag^+ – waste". All other aqueous waste can be poured into the sink under dilution with water.

After use, rinse all glassware with demineralized (WBI) water. If there are chemicals visible, rinse it with ethanol first and with demineralized (WBI) water. If this procedure is insufficient, clean it with soap water and a test tube brush, and then rinse it well with tap water followed by demineralized (WBI) water.

All single use plastic devices are collected in the chemical waste box.