Chlorate Titrations

Sodium Chlorate determination using Fe^{2+}/MnO_4^- system

Titration for solid sample

A solution of Ferrous Sulphate in water + acid (acid Ferrous Sulphate solution) is made up by dissolving 7.0 grams of Ferrous Sulphate Heptahydrate (3.83g Anhydrous FS) in 80ml freshly boiled distilled water + 5ml concentrated Sulphuric acid (add acid to water first). This solution (approx. 85ml) is made up to 100ml.
Make up a solution of 0.1N Potassium Permanganate (3.1608g per liter, 0.02M). You may need approx. 200ml per titration if you run a blank each time.
Obtain a 10% Manganous Sulphate (112g/l Monohydrate) solution.

Weigh accurately a 0.1g (Chlorate + other) sample (previously dried over conc. Sulphuric acid for 24 hours) and dissolve it in 10ml distilled water in a 250ml flask.
Add 35.0ml of the acid Ferrous Sulphate solution and boil gently for 10 minutes.
Cool, add 10ml of 10% Manganous Sulphate (112g/l Monohydrate) solution and titrate the excess Ferrous Sulphate with 0.1N Potassium Permanganate solution.
Run concurrently a blank with 35.0ml of the acid Ferrous Sulphate.

% $NaClO_3$ = [(A-B) x 0.17742/W]
where A = ml of K Permanganate solution used in blank, B = ml used in the sample test, W = weight of sample(use around 0.1g).

The above can be used for testing an unknown with a Chlorate content from zero to 100% Chlorate. If you are sure your solid sample contains a low percentage of Chlorate (say a sample from the end of a Perchlorate run) you may want greater resolution than what the above can offer. Take a larger sample size to titrate (say 1 gram as opposed to 0.1 gram) and proceed as above. The % Chlorate will now be :
%$NaClO_3$ = [(A - B) x 0.1772/1.0]
The 1g sample method will work OK so long as the percentage of Chlorate in the unknown is less than 15%, ie. from zero to 15% Na Chlorate.

The advantage of this system is that no redox indicator is needed. Chemicals are easy to obtain. The biggest problem is that Cl^- will interfere. This is prevented by adding $MnSO_4$ to the solution before titrating with K Permanganate.
Manganous Sulphate can be made with Sulphuric acid, K Permanganate and Oxalic acid. The $MnCO_3$ is then precipitated by adding $NaHCO_3$. The $MnCO_3$ was then washed and added to Sulphuric acid to give $MnSO_4$.
Note that it is **very** dangerous to add Sulphuric acid to solid K Permanganate, it should only be done in solution.
Ferrous Ammonium Sulphate Heptahydrate, $Fe(NH_4)_2(SO_4)_2{:}6H_2O$, (molecular weigh 392.2g) can be used instead of the Ferrous Sulphate and it is in fact better as it does not

get oxidized by Oxygen from the atmosphere. Use 9.8 grams per 100ml acid solution.
It may be difficult to weigh 0.1 gram of solid if you do not have an appropriate scales. Dissolving 5 grams solid in a solution made up to 250ml will give you 0.1 gram per 5ml. This will be easier to measure.
The procedure can be tested using pure K Chlorate which is easy to obtain pure by crystallization. Dissolve 11.5 grams K Chlorate in 500 ml solution and use 5ml to give the equivalent 0.1g of 100% pure Na Chlorate as above. Titrating this should give a result of 100%.
A redox indicator can be used in the above to more clearly show end points if you like. See here for more info on KMnO4 titrations.
Solutions of Permanganate and Fe Sulphate should me made up fresh as they do not keep well for long periods though they should be OK for a few months in tight capped bottles. Attempt to keep the Permanganate concentration as accurate as possible. Wash the container(s) for the Permanganate using a small amount of Permanganate solution before using them to get rid of organics. Make up more than one liter if you do not have appropriate scales. Use lab grade K Permanganate or recyrstallize to purify.

Reaction equations:
Chlorate is reduced by Fe^{+2} in known excess.

A: $6Fe^{+2} + 6H^{+} + (Cl^{+5}O_3)^{-} \text{------>} 6Fe^{+3} + Cl^{-} + 3H_2O$
$6FeSO_4 + NaClO_3 + 3H_2SO_4 \text{------>} 3Fe_2(SO_4)_3 + NaCl + 3H_2O$

The remaining Fe^{2+} is Oxidized by Permanganate

B: $(Mn^{+3}O_4)^{-} + 5Fe^{2+} + 8H^{+} \text{ ------> } Mn^{2+} + 5Fe^{3+} + 4H_2O$
$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \text{ ------> } 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$

There are more exacting titration procedures for Chlorate and Chloride in the Sodium Chlorate section under 'Collection of Graphs and Tables'.

Titration for cell contents

Use the titration below if you are dealing with liquid from Chlorate or Perchlorate cells.They are similar to the method above for a solid sample.
Estimate the amount of Chlorate per liter and use the appropriate sample size.

Sample sizes to suit different Chlorate concentrations are shown in the table.

Chlorate concentration grams per liter	Sample size (ml)
zero to 750	0.20
zero to 600	0.25
zero to 300	0.50
zero to 150	1.00

You will need:
A solution of Ferrous Sulphate in water + acid (acid Ferrous Sulphate solution) made up by dissolving 7.0 grams of Ferrous Sulphate Heptahydrate (3.83g Anhydrous FS) in 80ml distilled water + 5ml concentrated Sulphuric acid (add acid to water first). The solution (approx. 85ml) is made up to 100ml.
A 0.1N solution of Potassium Permanganate made by dissolving 3.1608 grams and making up to one liter (0.02 Molar solution).
A 10% Manganous Sulphate solution (112 grams Monohydrate per liter).

		Indicator if available. A few drops of 0.3% Methylene blue solution can be used if you wish, though it is not great when Perchlorate is present.
zero to 75	2.00	
zero to 15	10.00	

Take an appropriate sample size and add it to 10ml distilled water in a 250ml flask.
Add 35.0ml of the acid Ferrous Sulphate solution and boil gently for 10 minutes.
Cool, add 10ml of 10% Manganous Sulphate (112g/l Monohydrate) solution. (Add a few drops of indicator if you are using indicator). Titrate the excess Ferrous Sulphate with the 0.1N Potassium Permanganate solution. Add one cc of the Potassium Permanganate at a time so that a distinct colour change (red as contents are swirled if not using indicator) is seen at the end. When not using indicator the red colour does not persist for very long and the solution will go to a more dirty Orange color within 40 seconds or so. If you get a red colour that does not dissapear when you add the first ml of Permanganate, you need to use a smaller sample size from Chlorate cell.
Run concurrently a blank with 35.0ml of the acid Ferrous Sulphate.

$NaClO_3$ in grams per liter = [(A-B) x (1.7742/Sample size in ml)]

where A = ml of K Permanganate solution used in blank, B = ml K Permanganate used in the sample test.
Use a 1ml diabetic syringe (WITH a needle) if you do not have a 1ml pipette for the small sample sizes. 50cc syringes are OK for the Fe Sulphate and Permanganate solutions.
If taking samples from a cell to track CE make sure the cell volume is the same at each sampling time.
See notes above in relation to the K Permanganate solution (make it up as accurately as possible).

HIT THE BACK BUTTON ON YOUR BROWSER