

Potassium dichromate Potentiometric Titration of Iron in natural magmas

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Titration-Theory

gradual addition of an acidic solution to a basic solution or vice versa (see acids and bases); titrations are used to determine the concentration of acids or bases in solution. For example, a given volume of a solution of unknown acidity may be titrated with a base of known concentration until complete neutralization has occurred. This point is called the equivalence point and is generally determined by observing a color change in an added indicator such as phenolphthalein. From the volume and concentration of added base and the volume of acid solution, the unknown concentration of the solution before titration can be determined. Titrations can also be used to determine the number of acidic or basic groups in an unknown compound. A specific weight of the compound is titrated with a known concentration of acid or base until the equivalence point has been reached. From the volume and concentration of added acid or base and the initial weight of the compound, the equivalent weight, and thus the number of acidic or basic groups, can be computed. Instead of adding an indicator to observe the equivalence point, one can construct a graph on which the *pH* (see separate article) at regular intervals is plotted along one axis and the number of moles of added acid or base at these intervals along the other axis; such a plot is called a titration curve and is usually sigmoid (*S*-shaped), with the inflection point, where the curve changes direction, corresponding to the equivalence point. From the *pH* at the equivalence point, the dissociation constant of the acidic or basic group can be determined (see chemical equilibrium). If a compound contains several different acidic or basic groups, the titration curve will show several sigmoid-shaped curves like steps and the dissociation constant of each group can be obtained from the *pH* at its corresponding equivalence point.

Keywords: Potentiometric titration, iron (II), iron (III), potassium dichromate, hydrofluoric acid, sulphuric acid, boric acid

This method requires the use of concentrated sulphuric (H_2SO_4) and hydrofluoric acids (HF).

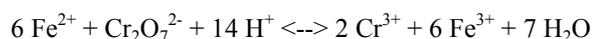
Weigh out a 75.00 +/- 0.01 milligrams of sample powder and transfer to a large teflon crucible and cover with teflon lid. Each of lids have two holes. One of them for inflow of CO_2 protect gas and second for outlet of vapour and excessive protect gas. Since we had three crucibles up to two samples and a standard can be analyzed as a batch, taking care not to mix up which sample is in which crucible. The first was analyzed a geochemical rock standard (as a standard has been used BHVO-1 standard from US Geological Survey, which is Hawaiian lava of known FeO concentration - 8,58 wt %).

Into each crucible with sample has been added ~3 ml deionized H_2O , 10 ml solution concentrated H_2SO_4 , HF and deionized H_2O in proportion 1:0,8:3. This solution was preparing before. To a 500 ml flask, 300 ml deionized H_2O , 100 ml concentrated H_2SO_4 and 80 ml concentrated HF were taken. The covered crucibles were moved to hot plate and stand for 30 minutes at very low boil under CO_2 gas protection, which was bubbled trough the solution before titration. After them were the crucibles moved to water bath for cooling, continuously under CO_2 gas. Approximately after 10 minutes cooling the crucible walls were washed down again with deionized H_2O and 10 ml of boric acid (H_3BO_3) was added. All samples disintegration was provided beneath the fume hood. Each crucible was transported to potentiometric titration with potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$).

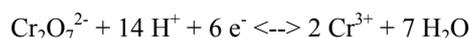
Iron may be determined by a redox titration with an oxidant such as KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$ that converts Fe(II) to Fe(III). Potassium dichromate can be used as a primary standard if it is dried in an oven at 150-200°C for two hours to remove any bound water. As the titration proceeds the sample solution will turn green due to the presence of Cr^{3+} . The endpoint is reached when the very fine yellow colour (at the beginning of titration curve) of

the Cr^{6+} titrant appears (at the end of titration curve). To prepare the 0.01N $\text{K}_2\text{Cr}_2\text{O}_7$ titrant, accurately weigh approximately 0.245 g of dry $\text{K}_2\text{Cr}_2\text{O}_7$ to the nearest 0.1 mg and place in a 500 ml volumetric flask. Dissolve in 300 ml of deionized water and dilute to volume. Calculate the normality of this solution based on six equivalents per mole of $\text{K}_2\text{Cr}_2\text{O}_7$.

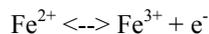
One of the most important types of analytical titrations involves oxidation-reduction reactions. In this experiment we titrated iron(II) solutions with a standard solution containing potassium dichromate ion to determine the percentage of iron in your unknown iron containing sample. The solution was then titrated with a standard potassium dichromate solution (0.01mol dm^{-3}) with titration rate 1.00 ml min^{-1} . Similarly, the potential values were recorded automatically when the potential change were within ± 2 mV min^{-1} for each additional. All titration were performed at 20 °C. The overall reaction is:



This reaction can be separated into two half-reactions. Dichromate ion acts as the oxidizing agent and its reduction can be written:



The iron(II) ion is oxidized to the iron(III) state by the dichromate ion:



After all the Fe^{2+} ion has been oxidized, the endpoint of the titration can be recognized by the colour change (from green to yellow) when excess dichromate ion now oxidizes.

A standard solution of known concentration is accurately prepared using solid $\text{K}_2\text{Cr}_2\text{O}_7$. This solution is then added

to a solution containing a known mass of an unknown iron salt until the endpoint of the titration is reached. For a redox titration, one equivalent of an oxidizing agent ($\text{Cr}_2\text{O}_7^{2-}$) reacts with one equivalent of a reducing agent (Fe^{2+}). From the half reaction for dichromate it can be seen that one mole of dichromate ion requires six moles of electrons. Therefore, the equivalent weight of $\text{K}_2\text{Cr}_2\text{O}_7$ is $(294.19 \text{ g/mole}) (1 \text{ mole}/6 \text{ eq.}) = 49.03 \text{ g/eq.}$ For Fe^{2+} the equivalent weight is $(55.847 \text{ g/mole})(1 \text{ mole/eq.}) = 55.847 \text{ g/eq.}$ The normality of the dichromate solution is six times its molarity.

Apparatus

All potentiometric titrations were performed using a **Dosimat 665**, Metrohm swiss automatic titrator. In the DOS dispensing mode, the balance connection allows direct calculation and display of the sample content. The 665 Dosimat accepts the sample weight directly and incorporates it automatically in the calculation formula. The built-in RS 232C interface allows the direct printout of the results. The CNT mode is used for the automatic preparation of solutions of specified content.



In the preparative laboratory, the DIS C mode is used for continuous dispensing. Two 665 Dosimats in tandem operation can be controlled via PC and thus allow uninterrupted dispensing. High accuracy of the dispensing and chemical resistance of the materials used allow universal deployment of the 665 Dosimat.

Efficient and precise pipetting or diluting in the PIP or DIL mode.

Metrohm Dosimat 665 was equipped with a combination platinum electrode (reference electrode is a **silver-silver chloride**) and E 649 Magnetic Swing-out Stirrer with electrode holder.



In the normal case the electrode should be filled with reference electrolyte $c(\text{KCl})=3 \text{ mol/L}$. The

electrolyte level should never be less than 1 to 2 cm below the fill hole. As a control unit was used 686 Titroprocessor, Metrohm with integrated, space-saving thermal printer (DIN A6). The titration vessel was a specially ordered five-necked flask (for micro-burette, electrode, thermometer and inlet and outlet of CO_2 gas).

Calculation

Weight % of FeO in samples is more less equal to volume of $\text{K}_2\text{Cr}_2\text{O}_7$ in ml multiply by 0,8.

To calculate the amount of Fe_2O_3 in own sample (not $\text{Fe}_2\text{O}_{3\text{Tot}}$), the computation is as follows:

Weight % of $\text{Fe}_2\text{O}_{3\text{Tot}}$ (from whole rock x-ray data or microprobe analysis) divided by 1.111348 is equal to weight % of FeO_{Tot}

Total weight % FeO_{Tot} minus % FeO (\pm titrated value) is equal to the amount of iron in the sample which really

exists as Fe_2O_3 (ferric iron). This needs to be multiplied by 1.111348 to re-convert back to the ferric oxide state (Fe_2O_3) and it should be listed as Fe_2O_3 on own summary analysis data sheet.

Application to natural magma samples

The proposed method was applied to the determination of iron(II) in standard BHVO-1 samples (USGS standard, Lit. 8,58 wt% FeO) and to the successive determination of iron(II) and iron(III) in a investigated natural magma samples. Decomposition of the former and latter samples was carried out according to the described procedures by using hydrofluoric, sulphuric and boric acid, respectively. The results obtained by the proposed method are given in Table 1. The analytical results were in good agreement with the certified values for standards. The method is alternative to the ^{57}Fe Mössbauer spectroscopic method. The results from this method are very useful to compare with results from ^{57}Fe Mössbauer spectroscopic method for achievement better accuracy.

Table 1 Determination of iron(II) in BHVO-1 standard from US Geological Survey, Hawaiian lava.

Measurement (date)	Proposed method, Fe(II) %		Certified values, Fe(II) %
	1 st end point	2 nd end point	
BHVO-1(01.4.01)	8,52	-	8,58
BHVO-1(05.4.01)	8,49	-	8,58
BHVO-1(05.4.01)	8,65	-	8,58
BHVO-1(25.4.01)	8,50	-	8,58
BHVO-1(26.4.01)	8,49	-	8,58
BHVO-1(31.5.01)	8,51	-	8,58
BHVO-1(31.5.01)	8,64	-	8,58
BHVO-1(20.6.01)	8,28	8,57	8,58
BHVO-1(22.6.01)	8,44	8,69	8,58
BHVO-1(23.6.01)	8,41	-	8,58

Titration as a method for total iron determination

By this method may be determined total iron also by a redox titration with an oxidants (KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$) that converts Fe(II) to Fe(III) as has been sad. However, in natural glasses iron typically occurs as Fe(III) and therefore must first be reduced to Fe(II) before the titration. In this experiment Fe(III) must be reduced with SnCl_2 followed by titration with $\text{K}_2\text{Cr}_2\text{O}_7$.

To receive an glass sample give your TA a weighing bottle in a labeled beaker. The sample should be dried at 105°C for at least one hour.

To prepare the 0.1N $\text{K}_2\text{Cr}_2\text{O}_7$ titrant, accurately weigh approximately 2.45 g of dry $\text{K}_2\text{Cr}_2\text{O}_7$ to the nearest 0.1 mg and place in a 500 mL volumetric flask. Dissolve in 300 mL of deionized water and dilute to volume. Calculate the normality of this solution based on six equivalents per mole of $\text{K}_2\text{Cr}_2\text{O}_7$. A fresh solution of the SnCl_2 reducing agent needs to be prepared each lab session. Dissolve 6 g of $\text{SnCl}_2 \cdot \text{H}_2\text{O}$ in 10 mL of concentrated HCl, using a 100 mL volumetric flask. After the SnCl_2 dissolves, dilute to volume. Keep this solution tightly sealed to prevent air oxidation.

Prepare the ore sample by dissolving an accurately weighed 0.3 g sample in a 250 mL Erlenmeyer flask containing 10 mL of concentrated HCl. Heat to near boiling, continuing until the sample is completely dissolved. All dark particles should be gone, but some

clear silicate particles may remain. Add enough SnCl_2 to turn this solution from yellow to clear (3-15 mL). Then, add 0.1N KMnO_4 dropwise until the solution just turns yellow.

A blank solution should be carried through the experiment in parallel with samples. The blank solution should contain 10 mL of HCl and 3 mL of the SnCl_2 solution. Add KMnO_4 until the color changes, then decolorize with SnCl_2 .

Carry samples through one at a time from this point on. Heat the solution nearly to boiling and add SnCl_2 dropwise until the yellow color disappears, then add two excess drops. Cool to room temperature and rapidly add 10 mL of the HgCl_2 solution that is provided. A small amount of white precipitate should be present. Add 10 mL of the HgCl_2 solution to the blank and carry it through the rest of the procedure as if it were a sample.

Add 10 mL of concentrated H_2SO_4 and 15 mL of concentrated H_3PO_4 , cool, and then add 8 drops of sodium diphenylamine indicator.

Titrate with 0.1N $\text{K}_2\text{Cr}_2\text{O}_7$. The endpoint is the first permanent appearance of a violet-blue color. During the titration the solution will turn green due to the presence of Cr^{3+} ion. Keep titrating until it turns dark violet-blue.

Report the percentage of Fe in the ore sample.

NOTE: Solutions containing Cr or Hg should not be poured down the sink, since these metals are highly toxic. Dispose of these solutions in the waste containers that are provided.

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