

FeO determination in rocks and minerals by wet chemistry

Introduction

Most analytical techniques used for rocks and minerals cannot distinguish between the oxidation states of different chemical elements, including iron. Because of its abundance, the redox state of iron can be particularly important. The iron in common rocks is in the Fe^{2+} and Fe^{3+} states, usually present in minerals as the nominal chemical components FeO and Fe_2O_3 , respectively. The analytical procedure described here permits the analysis of FeO in a sample by titration.

How it works

1. The powdered sample is dissolved with **HF** at room temperature in a plastic container. Dissolution occurs in the presence of excess V^{5+} . V^{5+} oxidizes the Fe^{2+} to Fe^{3+} as it is released from the minerals, while vanadium is reduced to V^{4+} . Oxidation of Fe^{2+} by air is rendered unimportant, and fortunately the reoxidation of V^{4+} back to V^{5+} by air is very slow.
2. V^{5+} remaining after dissolution is titrated using a standardized Fe^{2+} solution.
3. Initial moles V^{5+} - final moles V^{5+} = moles Fe^{2+} in sample.

This procedure can easily yield accuracy and precision of ~1%, but it is subject to interference from other reduced species such as Mn^{2+} and sulfide. This method will not dissolve some Fe-bearing minerals such as chromite. Consult a geochemical methods text for a detailed discussion of analytical concerns. Though not especially complicated, this procedure involves the usual calculations involving volumes, weights, molecular weights, and moles. All of the calculations are given on [this spreadsheet](#).

One warning is that the titration is done in **HF**. You absolutely must take all reasonable **precautions** including wearing safety clothing, plastic or rubber gloves, goggles or a face mask, and you must have the hood fan turned on and sash as low as is convenient. This method is designed for approximately 40-50 titrations.

Table 1. Atomic and formula weights.

Compound	Formula weight	Notes
H	1.00794	Atomic weight
N	14.0067	Atomic weight
O	15.9994	Atomic weight
S	32.066	Atomic weight
K	39.0983	Atomic weight
V	50.9415	Atomic weight
Cr	51.996	Atomic weight
Fe	55.847	Atomic weight
FeO	71.8464	Nominal Fe^{2+} component in minerals
NH_4VO_3	116.97816	V^{5+} oxidant during sample dissolution
$\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	392.1428	Fe^{2+} titrating solution
$\text{K}_2\text{Cr}_2\text{O}_7$	294.1844	Standard for calibrating the Fe^{2+} titrating solution

The following table summarizes the different solutions and materials needed.

Table 2. The solutions needed.

What's needed	Material	Amount	Units	Notes
Fe ²⁺ in rock	Rock sample	0.200	g	Sample weight around which these calculations are made.
	FeO maximum	15	%	FeO in rocks is rarely higher than this. Adjust sample weight, on the line above, as necessary for your own samples.
	FeO present	0.0300	g	Typical maximum FeO 15%
	Fe ²⁺ present	0.0233	g	-
	Moles Fe to oxidize	0.000418	moles	-
V ⁵⁺ solution	Moles V ⁵⁺ needed	0.00060	moles	~50% excess over highest expected Fe ²⁺ concentration
	Solution volume	0.002	liters	Add 2 ml of solution to the sample
	Solution concentration	0.3	molar	Required V ⁵⁺ concentration
	NH ₄ VO ₃	35.1	g/liter	-
Fe ²⁺ solution	Ferrous solution	25	ml	Titration solution
	Fe ²⁺ needed	0.00065	moles	With a burette volume of 25 ml, this gives a slight excess of Fe ²⁺ titrant over the maximum possible amount of V ⁵⁺ that must be titrated.
	Solution molarity	0.026	moles/liter	-
	Fe(NH ₄) ₂ (SO ₄) ₂ •6H ₂ O	10.20	g/liter	-
Dichromate solution	Fe ²⁺ in burette (Fe ²⁺ solution from above)	0.00065	moles	Titration solution
	Dichromate needed	0.0000975	moles	Moles dichromate is 1/6 that of moles Fe ²⁺ , because Fe ²⁺ = Fe ³⁺ + 1e ⁻ , compared to 2Cr ⁶⁺ + 6e ⁻ = 2Cr ³⁺ (note that the 2 in 2Cr is the di- in dichromate). The amount of dichromate is needed is actually 10% less, to assure that the 25 ml of Fe ²⁺ solution in the burette can reach the end point.
	Dichromate needed	0.0287	g	-

Analytical procedure

Analysis takes two or three days. On the first day sample dissolution is started. On the second or third day the titration can be done. Because the Fe²⁺ is generally in dark minerals, when the dark stuff is gone the digestion is probably done. Ignore the insoluble Al, Mg, and Ca fluoride salts, they don't make any significant difference to Fe²⁺ determination. At least they

don't seem to. Calculations can be done when you are finished with the titrations. The following three tables give the complete procedure. In general, it is best to process all samples through each step before proceeding to the next step.

Day 1

Table 3. Procedures that can be done on the first day.

Step	Do these things	Notes
H ₂ SO ₄ solution	<p>Fill a 2 liter plastic bottle 3/4 full with deionized water. Put it in a cold water bath (e.g., the sink).</p> <p>Add to the bottle 535 ml (~980 grams) of concentrated H₂SO₄ (~5 M)</p> <p>Let the bottle cool, then mix, cool again, and dilute with DI water to fill the bottle.</p>	<p>To help keep transition metals in solution and not as solid fluorides.</p> <p>Exact amount not critical.</p> <p>Exact concentration not critical. DO NOT use a volumetric flask.</p>
V ⁵⁺ solution	<p>Fill a 100 ml volumetric flask half full with the H₂SO₄ solution.</p> <p>Add 3.51 g of NH₄VO₃ powder.</p> <p>Swirl till dissolved, then dilute to volume with the H₂SO₄ solution.</p>	<p>-</p> <p>-</p> <p>-</p>
Digesting sample	<p>Weigh 0.200 +/-0.01 g sample into a clean polystyrene vial</p> <p>Add 2 ml of the V⁵⁺ solution, swirl to mix</p> <p>Add 4 ml of HF, swirl to mix</p>	<p>Record weight to the full precision of the balance. In addition to the samples, make at least 3 blanks (no sample in the vials).</p> <p>Powder must be dispersed before HF dissolution begins, otherwise fluoride salts cement the mass into a lump.</p> <p>Dissolution now begins. Replace the vial cap. Let stand for 1-2 days in the dark (under a box, for example; we don't want any photo-oxidation now, do we?).</p>
Redox indicator solution	<p>In 100 ml of deionized water add 0.2 g of Ba-diphenylamine sulfonate. Swirl to dissolve.</p>	<p>May take a while to dissolve. Volumetric flask not necessary.</p>

Day 2 or 3, depending on how long digestion takes

Table 4. These procedures should be done on the day of the analysis, which should not follow the start of dissolution by more than 2 days.

Step	Do these things	Notes
Dichromate solution	Dry the $K_2Cr_2O_7$ powder at $150^\circ C$	To remove traces of adsorbed water.
	Weigh 0.0287 +/-0.001 g of potassium dichromate into a polystyrene vial	Record the weight of the powder to the precision limit of the balance. This is Value A used below.
	Add 2 ml of the H_2SO_4 solution.	-
Fe^{2+} solution	Fill a 1000 ml volumetric flask half full with the H_2SO_4 solution.	-
	Add 10.2 g of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ powder, swirl to dissolve.	-
	Fill to volume with the H_2SO_4 solution.	-
Calibrate the Fe^{2+} solution	Fill the burette with Fe^{2+} solution.	Be sure beforehand that the burette is clean and well-rinsed. HF in the solution will etch the glass burette tip, making it a pain to use. Put a small diameter plastic tube on the tip to protect it.
	Add 0.5 ml of the indicator solution to the dichromate solution	-
	Add a stirring bar and start the stirring	Stirring bar should be clean.
	Titrate the chromate standard solution to the end point	The orange dichromate solution gradually turns brownish, then to greenish as Cr^{3+} replaces Cr^{6+} . As it becomes green, suddenly the dark blue color of the indicator starts to show. The end point is a light blue color, probably appearing blue-green. The volume of titrant used is Value D, used below.
Titrate the blanks and samples	Re-fill the burette with ferrous sulfate solution	-
	Add 0.5 ml of the indicator solution to the sample or blank solution	-
	Add a stirring bar and start the stirring	Stirring bar should be clean.
	Titrate the solution to the end point	Light blue end point. The volumes of titrant used is recorded for each sample, are the F values used below.

Calculations

Table 5. Calculations after analyses are complete. Again, [this spreadsheet](#) has the calculations built in.

Calculation	Item	Values	Units	Notes
Calibration calculations	Weight dichromate	A	g	From Day 2 or 3 tasks
	Moles dichromate weighed	$B = A/294.1844$	moles	Calculation
	moles Fe^{2+} , iron titrant solution used	$C = B*6$	moles	6 e ⁻ released for each dichromate reduced
	Volume Fe^{2+} titrant solution used to titrate dichromate solution	D	ml	From Day 2 or 3 tasks
	Moles Fe^{2+} per ml of solution	$E = C/D$	moles/ml	Calculation
Initial blank and sample calculations	Volume of Fe^{2+} titrant solution used, value F different for each blank and sample	F	ml	From Day 2 or 3 tasks, value F different for each sample and blank
	Moles Fe^{2+} in titrant used	$G = F*E$	moles	Each sample and blank has its own G result
Calculate the average blank	Average of moles Fe^{2+} in titrant for all blanks	H	moles	Calculation using all blank values of G above
Calculate the amount of FeO in the samples	moles Fe^{2+} in titrant used	G	moles Fe^{2+} in titrant	From above for each sample (not blanks)
	moles Fe^{2+} in sample	$J = G-H$	moles consumed for a sample	Amount of Fe^{2+} actually in the sample (= V^{5+} reduced), blank corrected
	Grams iron oxidized	$K = J*55.847$	g	moles Fe^{2+} to grams Fe^{2+}
	Grams FeO oxidized	$L = K*1.2865$	g	Grams Fe^{2+} to grams FeO
	% FeO in sample	$M = 100*L/\text{sample weight}$	weight %	Weight % FeO in sample

There, wasn't that easy?