

A CONTRIBUTION TO THE DETERMINATION OF MANGANESE IN SILICATES

BY

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WITH 1 FIGURE IN THE TEXT

The usual method of determining manganese in silicates is a colorimetric comparison of KMnO_4 with a standard solution after oxidizing with KJO_4 (1). This method works fairly well when the amount of manganese to be determined does not exceed 0.5% of the silicate. For larger quantities it is not adequate since the determination of aluminium by difference depends upon an accurate determination of manganese and iron.

During an investigation by mag. scient. H. Neumann on Kongsberg minerals I had the pleasure of doing some mineral analyses, partly independant and partly together with him. Amongst others I had the opportunity of analysing a specimen of axinite, which, containing nearly 4.5% MnO , at once confronted me with the above problem. In this case the first difficulty was to decide in which stage of the analyses the precipitation of manganese should be effected. (It was at once evident that this amount could not be determined colorimetrically in the usual way.) The common method of precipitating manganese together with the sesquioxides after oxidizing with bromine-water is not recommendable in this case since contamination with calcium and magnesium is apt to occur (2).

Different procedures were tried: For instance a colorimetric determination of the manganese that was precipitated with the sesquioxides without oxidation with bromine water, and a subsequent determination of the chief amount of manganese (precipitated as sulfide from an acetic acid solution) (3). Or precipitation of manganese with "oxin" (4). But none of these methods were satisfactory.

Then I came across a paper by H. Lang and F. Kurtz on the determination of manganese (5). And the method suggested by these authors proved to be highly suitable for silicate analysis.

I shall give a brief account of the principles involved: Mn^{2+} is oxidized to Mn^{7+} with $\text{K}_2\text{S}_2\text{O}_8$ and AgNO_3 as a catalyzer. Some HPO_3 is added to make the oxidizing process irreversible. Mn^{7+}

is now titrated with Fe^{2+} using diphenylamine as indicator. This indicator gives a very distinct and sudden change of colour turning from dark blue-violet to light green. At the end point the change takes place with half a drop $n/50 \text{ Fe}^{2+}$ (0.02 ml).

To test the method the following solutions were prepared:

- I. 3.9508 g KMnO_4 solved in water reduced with SO_2 filled up to 500 ml
- II. 0.6585 » » » » » » » » » » 250 »
- III. 1.5803 » » » » » » » » » » 500 »
- IV. Contains ca. 0.1 mg MnO per ml.

The FeSO_4 -solutions are prepared in large store-bottles (10 l). One $n/10$ and another $n/50$ and are kept under CO_2 -pressure.

A good arrangement is shown in fig. 1. Solutions kept in this way preserve nearly constant titer for years.

The FeSO_4 -solutions are adjusted against $\text{K}_2\text{Cr}_2\text{O}_7$. It is necessary to add ca. 5 ml H_3PO_4 (sp. w. 1.7) to each sample, to make the change of colour more distinct.

Procedure: To the solution which must not contain Cl^- -ions ca. 10 grams of HPO_8 is added and it is warmed until this is dissolved. Then 10 ml $n/10 \text{ AgNO}_8$ and ca. 2 grams of $\text{K}_2\text{S}_2\text{O}_8$ dissolved in a small amount of water are poured in. It is good to add two or three small peces of glass-capillars to prevent bumping. The solution is kept at a boil for 20 minutes to destroy excess of $\text{K}_2\text{S}_2\text{O}_8$, cooled under the tap, titrated to pink. Now 2 or 3 drops of as olution of diphenylamin in phosphoric acid is added and the titration is continued till the solution turns green.

The results of test-analyses are tabulated below:

Mn-solution I:	$n/10 \text{ FeSO}_4$	Calculated	Error %
	24.57 ml	} 24.53 ml	0.2
	24.58 -		0.2
	24.58 -		0.2
	49.36 -	} 49.35 -	0.0
	49.35 -		0.0 added 3 g CaO
	49.37 -		0.0 - 3gMgO

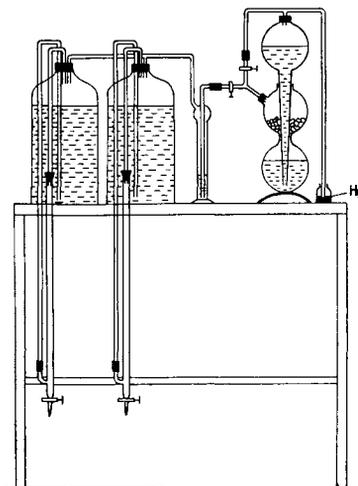


Fig. 1. Arrangement for titration of manganese

Mn-solution II:	n/10 FeSO ₄	Calculated	Error%
	16.47 ml		0.1
	16.47 -		0.1
	16.41 -	} 16.46 ml	-0.3
	16.47 -		0.1
	16.57 -		0.7
	16.50 -		0.2
	20.53 -	 20.61 -
Mn-solution III:	19.78 -	} 19.74 -	0.2
	19.73 -		-0.1
Mn-solution IV:	n/50 FeSO ₄		
	8.80 ml added ca. 20 mg TiO ₂		
	8.79		
	24.74		
	24.72		
	24.72 - added ca. 20 mg TiO ₂		

The determination of Manganese in silicates can be done in two ways. Either precipitate manganese together with the sesquioxides after oxidizing with bromine-water, or let manganese distribute itself among this and the following precipitates. Then some of it will be co-precipitated with the sesquioxides, some together with calcium, and the chief amount will appear as phosphate together with magnesium. However, manganese is not quantitatively precipitated in this way (6), and the filtrate must be evaporated to dryness, Cl⁻-ions driven off by repeated evaporations with nitric and sulfuric acids and manganese determined in the residue.

In a common rock-analysis where the amount of manganese does not exceed 0.5% the first method is sufficiently accurate. Then the sesquioxides are fused with K₂S₂O₇ in the ordinary way and an aliquot part is taken out (1/5 is sufficient) for the determination of manganese.

If greater amounts of manganese is present as the case was with the axinite, it is better to let manganese disperse. Manganese in the sesquioxides is determined as just described. The precipitates of CaO and Mg₂P₂O₇, after having been weighed, are dissolved in H₂SO₄ and manganese oxidized and titrated as mentioned above.

The chief objection to this method is that both calcium and magnesium are determined indirectly. But in this case it will not involve any great error since manganese is weighed as the well defined Mn₃O₄ and Mn₂P₂O₇, respectively, and the subsequent determination of manganese can be conducted with great accuracy.

In the table below I give the distribution of manganese in the different precipitates during the analyses of the axinite.

	I	II
In sesquioxides	0.63 %	0.53 %
» Ca-precipitate	0.67 -	0.44 -
» Mg-precipitate	3.00 -	3.22 -
» filtrate	0.12 -	0.24 -
Sum	4.42 %	4.43 %

For more than a year this method of determining manganese in rocks has been used with great advantage in the laboratory of the Mineralogical Institute. In regard to both time and accuracy it is preferable to the colorimetric methods now generally applied by silicate chemists.

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