

## **ANALYTICAL METHODS OF MANGANESE ORES I.**

Separation of iron, aluminum, manganese, calcium and magnesium by ion exchange method and their complexometric determination

GY. GRASSELY

Institute of Mineralogy and Petrography,  
University of Szeged

### INTRODUCTION

Intending to carry out the analysis of manganese oxide ores, the following components are to be determined in general:  $\text{MnO}$ ,  $\text{O}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{BaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{SiO}_2$ ,  $\text{P}_2\text{O}_5$ ,  $\text{CO}_2$  (carbonate), C (organic),  $\text{H}_2\text{O}$ , S. Beside the components mentioned sometimes the determination of copper, lead, cobalt, nickel and occasionally that of the arsenic and zinc is needed.

The analysis of oxide manganese ores is not one of the simplest tasks of ore analysis, among others, due to the great number of the components, even taken into account the components generally to be determined.

The modern, instrumental analytical methods, the rapid determinations worked out by combination of complexometric ones and ion exchange technique are more and more gaining ground in the field of the silicate analysis, mentioning merely the well known papers of SHAPIRO, BRANNOCK and RILEY, respectively [1956, 1958]. These methods offer the possibility to carry out precisely numerous silicate analyses within a relatively short time.

The analysis of manganese oxide ores can not be considered a simpler task than that of the silicates. Though, during the daily routine analyses of manganese ore mines the determination of moisture,  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MnO}$  and  $\text{P}_2\text{O}_5$  content is generally sufficient from the point of view of the practical valuation of the ores, among other practical viewpoints the geochemical study of the manganese ore deposits necessitates to have rapid analytical methods for the analyses of manganese ores as in the case of silicates securing the accuracy, the rapidity and the possibility of furnishing of numerous data in relatively short time.

It seems to be useful to examine the possibilities of applying of the ion exchange technique for the separation of some major components followed by their complexometric determination.

## THE POSSIBILITIES OF THE SEPARATION OF IRON-ALUMINUM-MANGANESE-CALCIUM-MAGNESIUM

The application of ion exchangers as well as that of the suitable complexing agents furnishes different possibilities of the separation. These methods can be divided into two groups in general: in the first group anion exchangers in citrate form are used, then the cations forming citrate complexes remain in the resin bed, whereas the others pass into the effluent. This method is applied by SAMUELSON, LUNDÉN and SCHRAMM [1952, 1953] to separate alkalis and alkali earth metals from the other metals and similarly this is the essence of the separation of the alkalis in the RILEY's rapid silicate analysis [1958].

In the second group methods using cation exchangers in hydrogen or sodium cycle can be arranged. Adding to the influent complexing reagents forming stable complexes with iron, aluminum, (titanium) at a definite pH, these components as stable complexes pass through the resin bed, whereas the others remain in the bed and they can be selectively eluted from the bed and finally in the effluent they can be determined.

From the point of view of our task the methods of the latter group seemed to be more convenient. USATENKO and DATSENKO [1948] used cation exchanger (Wofatit KPS 200 in hydrogen form) to determine the calcium and magnesium content of iron ores. The iron and aluminum were complexly bound by addition of citric or tartaric acid, passing thus into the effluent, whereas the calcium and magnesium were taken up quantitatively during the passage. After elution with dilute hydrochloric acid, calcium and magnesium were determined in the acidic solution.

Similar is to this the method for separation of iron — manganese — magnesium according to oral communication of Miss V. TOLNAY and Mrs. STEFANIA RAPP. By this method citric acid is added to the solution to be analyzed containing iron, manganese and magnesium and the solution buffered to pH 3,5 is introduced into the column containing cation exchanger in sodium form. The iron passes through the resin bed as citrate complex, the manganese and magnesium are bound in the bed. The manganese can be eluted by known excess of disodium EDTA at pH 4,7 and after washing of the resin bed, the elution of the calcium follows with known excess of EDTA at pH 11.

FRIESE [1960] proposed a method for separation of iron — aluminum — calcium — magnesium firstly at the rapid analysis of furnace slags. It is used Wofatit KPS 200 cation exchanger in sodium form. EDTA is added in known excess to the solution introduced into the top of the column, adjusting the pH of the influent to 4. Calcium and magnesium remain in the resin bed, iron and aluminum as  $FeY^-$  and  $AlY^-$  pass through the column. The excess of EDTA in the effluent containing iron and aluminum is titrated with zinc acetate solution at pH 5 against diphenylcarbazone — vanadium-EDTA-complex indicator, determining thus the sum of iron and aluminum. The iron content will be determined in an aliquot of the stock solution to be analyzed by direct titration with EDTA at pH 2,5 against sulfosalicylic acid indicator. The calcium and magnesium are eluted together with known excess of EDTA at pH 11. Firstly the sum of calcium and magnesium is determined in the

effluent titrating back the EDTA excess with zinc acetate solution and after separating the calcium as oxalate, the precipitate is filtered off and after ignition the calcium oxide will be dissolved in dilute hydrochloric acid and the calcium is determined complexometrically in presence of magnesium-EDTA complex against Erioblack T indicator.

The last mentioned methods formed essentially the base of our investigations, whose aim was to find the most suitable conditions securing accuracy and reproducibility in the case of analyses of manganese ores.

The separation and determination, respectively, of iron — aluminum — manganese — calcium — magnesium content of oxide manganese ores can be carried out accurately and relatively simply according to our experiences and using ion exchange columns in adequate number the rapidity of the determinations is essentially higher than that of the methods applying classical ones.

## EXPERIMENTAL RESULTS

### 1. Decomposition of the samples

Taking into considerations that ion exchange resin is used to separate the components mentioned, such a decomposition method can be applied, which secures that the concentration of the solution falls within the limits adequate to the ion exchange technique further that the solution introduced into the column does not contain any silica.

Therefore, the rapid decomposition method by potassium hydroxide suggested by SAJÓ [1955] else proved to be very convenient can not be taken in account, nor can be applied the simple decomposition by dilute hydrochloric acid containing hydrogen peroxide applicable for decomposition of pure manganese oxides, since the silica in various amounts in some form is nearly always present in sedimentary manganese oxide ores.

Combination of two methods seemed to be purposeful: first the manganese oxide components of the sample are to be dissolved by dilute hydrochloric acid containing a few hydrogen peroxide then the solution together with the insoluble residue is washed into a Pt-dish, the solution is evaporated and the silica is removed by treatment with hydrofluoric acid finally the traces of hydrofluoric acid is driven off by repeated evaporations with concentrated hydrochloric acid.

The single steps of the decomposition are as follows:

a) 1 g of finely powdered sample is weighed in a beaker of 250 ml, 50 ml 1 : 1 hydrochloric acid and 5—6 ml 30% hydrogen peroxide is added, the beaker is covered and heated on water bath till the decomposition of manganese oxides. If needed, the solution is kept cooling a while and further 1—2 ml hydrogen peroxide is added to the solution until the manganese oxides fully decompose. Finally the solution after a short boiling is poured and washed into a Pt-dish together with the insoluble residue.

b) 15—20 ml hydrofluoric acid of 40% is added to the solution and evaporated to dryness on the water bath.

c) 15—20 ml hydrochloric acid is added into the dish and evaporated. This step is repeated.

d) 5 ml hydrochloric acid and 30–40 ml deionized water is added into the dish, heated a while on the water bath, then poured into a beaker, boiled and after cooling the pure solution is poured into a 500-ml flask and filled up to the mark with deionized water. Aliquots of 50 ml of this solution are used for the separation and determination of the components in question.

## 2. Data of the exchanger bed, the conditions of the separation

Wofatit KPS 200 cation exchanger is used for the separation. The resin — after suitable grinding and sieving (particle size 0,2–0,4 mm) and purification — is transformed to sodium cycle by treatment with sodium chloride solution of 5% and finally washed chloride-free with deionized water. The inner diameter of the column is 23 mm, its height 170 mm and the height of the resin bed is 100 mm.

The solutions to be analyzed as well as the elutriants adjusted to suitable pH are generally introduced into the columns by completing to 100 ml. The volume of the washing liquid (deionized water) was in general 150 ml introducing it in parts of 25 ml.

The flow rate of the solutions as well as that of the first 100 ml of the washing liquid is generally 1,5 ml/min., the flow rate of the further 50 ml of the washing water may be somewhat greater.

To obtain accurate results all the solutions are to be prepared with deionized water.

## 3. The separation and determination of iron, aluminum, manganese, calcium and magnesium in manganese ores

### a) Separation of iron and aluminum from manganese, calcium and magnesium

To the aliquot of 50 ml of the solution to be analyzed 0,05 M EDTA is added in known amount in order to have it in about 30 per cent excess related to the sum of iron and aluminum content to be expected as it is mentioned by FRIESE [1960]. The pH of the solution is adjusted to 3,5 with acetate buffer and boiled for 3 minutes, cooled and introduced into the column rinsing the beaker carefully. Iron and aluminum pass through the resin bed and get into the effluent, manganese, calcium and magnesium are quantitatively taken up in the resin bed. Following the percolation of the solution of 100 ml the column is washed with 150 ml water.

The adjustment of pH to 3,5 is essential owing to the accurate separation. FRIESE could carry out the separation of iron and aluminum from calcium and magnesium also at pH 4, in our case — considering the presence of manganese — the separation at pH 3,5 is surer taking into consideration that the manganese already at pH 4,7 can quantitatively be eluted with EDTA from the resin bed. Therefore, introducing the solution with EDTA excess at pH 4, it may occur the danger that traces of manganese would get into the effluent.

The boiling of the solution is also essential to secure the formation of stable aluminum-EDTA complex at the given pH. Not boiling the solution

a part of aluminum might not get into the effluent but would remain in the resin bed.

The too great excess of EDTA is, however, to be avoided. The excess should not be the manyfold quantity of EDTA needed to bind the sum of iron and aluminum present. Ideal is the smallest possible excess; the 80–100% excess should not be surpassed. Consequently, it is proper to take 50 ml aliquots from the solution to be analyzed before separation, the pH is adjusted to 2,5 and the iron is titrated directly with 0,05 M EDTA against sulfosalicylic acid indicator. So the volume of 0,05 M EDTA needed to bind the iron contained in the 50 ml aliquot is determined, whereas the estimated amount of the insoluble residue observed at the decomposition of the sample may furnish at least approximate information concerning the aluminum content to be expected, if the residue consists of mainly alumo-silicates.

### b) *Determination of iron and aluminum*

The effluent of 250 ml contains the iron and aluminum, whose sum is determined by back titration of the EDTA excess with 0,05 M zinc acetate solution.

FRIESE used diphenylcarbazone — vanadium-EDTA complex indicator at the back titration; whereas benzidine — potassium ferrocyanide — ferricyanide indicator system is suggested by SAJÓ [1955].

It was found during our investigations that the xylenol orange indicator can very conveniently be applicated instead of the indicators mentioned at the back titration of the EDTA excess with zinc acetate solution at pH 5,5–5,6. The end point is very sharp, the color turns from yellow to cyclamen red.

The procedure is as follows:

The effluent of about 250 ml is evaporated to 150 ml on water bath, after cooling hexamethylenetetramine is added adjusting the pH to 5,6, then xylenol orange indicator (in aqueous solution or in solid state as finely powdered mixture of indicator and potassium nitrate) is added as long as the solution obtains a pronounced yellow color. The EDTA excess is titrated with zinc acetate solution to the sharp end point. From the consumption the volume of 0,05 M EDTA equivalent to the sum of iron and aluminum present is to be calculated. Then 30 ml of saturated sodium fluoride solution is added to the solution titrated, boiled for 3 minutes, cooled (the color somewhat changes due to the shift of the pH), the pH is anew adjusted to 5,6 with a few drops of dilute hydrochloric acid (the color turns again yellow), a small amount of indicator is added to the solution and the EDTA liberated in consequence of the precipitation of aluminum as sodium aluminum fluoride is titrated with zinc acetate solution. From the difference of the two titrations the iron content is to be calculated.

Results of successive determinations of iron and aluminum in the same solution according to the procedure mentioned are given in **Table 1**. The solution is prepared as follows: 1 g of a manganese ore sample from Urkut is decomposed as described then stock solution of 500 ml is prepared. The separation and determination of iron and aluminum was carried out in aliquots

of 50 ml and 25 ml, respectively, of this stock solution. The results in **Table 1** are referred to 50 ml aliquots, hence the iron and aluminum content of the sample can be given directly in per cent.

**Table 1**

Successive determination of iron and aluminum in the same solution according to the method described

	mg Fe	mg Al	
	found in the effluent after separation of iron and aluminum from manganese, calcium and magnesium by cation exchanger		
$s = \pm 0,0547$ mg	3,29	0,49	$s = \pm 0,0305$ mg
$s_x = \pm 0,0149$ mg	3,12	0,52	$s_x = \pm 0,0101$ mg
$C = 1,70\%$	3,20	0,54	$C = 5,76\%$
$E = 0,56\%$	3,20	0,48	$E = 1,92\%$
	3,26	0,55	
	3,21	0,52	
	3,23	0,52	
	3,23	0,52	
	3,12	0,58	
	3,24	0,56	
average	<hr/> 3,21 mg Fe	<hr/> 0,53 mg Al	

The determination of iron and aluminum can also be carried out in a way that the EDTA excess in the effluent containing iron and aluminum is determined by back titration with zinc acetate solution against xylenol orange indicator, so determining the sum of the two components and the iron content is determined by direct titration in single parts of 50 ml of the stock solution as usual against sulfosalicylic acid indicator. From the difference of the consumptions of the two titrations the aluminum content can be calculated. The data concerning the aluminum determinations in the proof analyses in the Appendix are obtained in this way.

c) *Separation of manganese from calcium and magnesium, determination of manganese*

Having separated the iron and aluminum from the other components first the manganese has to be eluted with 0.05 M EDTA solution used in known excess of 100–120% related to the volume of EDTA needed to bind the manganese to be expected. A greater excess is needless, whereas less under such experimental conditions is not sufficient to elute quantitatively the manganese. To the necessary volume of the EDTA 10 ml acetate buffer of pH 4.7 is added introducing this solution into the column, rinsing the beaker repeatedly with water, till the volume of the elutriant reaches about 100 ml.

Informations concerning the effect of the employed EDTA excess on the quantitiveness of the elution of the manganese are given in Table 2.

Table 2

mg Mn added in the influent	mg Mn found in the effluent employing at the elution		
	50%	100% EDTA excess	150%
50.32	44.66	50.13	50.35
	44.36	50.38	50.43

In the effluents eluted with 100% and 150% excess, respectively, the mean value of the determined manganese is 50.32 mg, while the EDTA excess of 50% proved to be insufficient for quantitative elution of manganese added into the influent. In such cases the error is doubled, partly a lower manganese content is obtained and on the other hand the manganese remained in the column will be eluted together with the calcium and magnesium at pH 11 thus falsifying the results of the determination of the latter two components too.

In a manganese oxide ore sample from Urkut the following manganese content could be determined by the method mentioned in ten parallel determinations.

% Mn		
53.29	53.23	$s = \pm 0.1435 \text{ mg}$ $s_x = \pm 0.0478 \text{ mg}$ $C = 0.269\%$ $E = 0.089\%$
53.29	53.40	
53.23	53.34	
53.34	53.62	
53.50	53.12	
av. 53.33%		

The manganese content of the aliquots of the solutions used for proof analyses varied between 4–30 mg and to elute such amounts of manganese equally 25–25 ml 0.05 M EDTA was used.

Having percolated the elutriant through the column, the resin bed is washed as usual and a little ascorbic acid and 5 ml  $\text{NH}_3\text{--NH}_4\text{Cl}$  buffer is added to the effluent of 250 ml and the excess of EDTA is titrated with zinc acetate solution against Erioblack T indicator.

d) *Elution and determination of calcium and magnesium*

The elution of calcium and magnesium is carried out together by 0.05 M EDTA solution in known excess, buffered to pH 11, as it is proposed by FRIESE [1960]. According to FRIESE about 50% excess of EDTA is to be used to secure a quantitative elution. In our other experimental conditions seemed to be purposeful to apply the EDTA in 100% excess.

The EDTA excess in the effluent is determined by back titration with zinc acetate solution against Erioblack T at pH 10, calculating from the consumption the volume of EDTA equivalent to the sum of calcium and magnesium.

After having determined the volume of EDTA equivalent to the sum of calcium and magnesium, the solution is acidified to pH 5–6 with dilute hydrochloric acid and evaporated on water bath to a volume of about 150 ml and after adding 0.5 g ammonium acetate and 3–4 ml acetic acid, is boiled and while boiling 30 ml also boiling ammonium oxalate solution of 3.5% is poured to the solution and is heated on water bath for an hour, then kept for a few hours. The filtered and washed calcium oxalate precipitate is ignited, the calcium oxide is dissolved in a few dilute hydrochloric acid, the content of the crucible is poured and washed into the beaker used for the precipitation. To remove the bulk of the acid, the solution is evaporated but not to full dryness. 100 ml water is added into the beaker and the pH is adjusted to 11–12 by freshly prepared, carbonate-free sodium hydroxide solution of 2% and then the calcium is determined by direct titration with 0.05 M (or 0.01 M) EDTA solution against Erioblue SE indicator to the sharp end point (the color turns from red to blue or violet blue). Concerning the experiences referring to the Erioblue SE indicator in connection with the calcium determination in the presence of magnesium see publication of G. KOVÁCS and K. TÁRNOKY [1959].

The advantage of using Erioblue SE is that it does not react with the magnesium, therefore, the titration gives accurate results in that cases too if a small amount of magnesium would be co-precipitated with the calcium oxalate. The method outlined above is mainly proposed if the calcium and magnesium content to be expected is relatively low.

Should the calcium and magnesium content amount to more mgs the way may be followed: the percolating solution drops immediately in a 250-ml flask and after having washed the column with 130 ml water the solution is filled up to the mark. In 100 ml of this solution the sum of calcium and magnesium is determined as usual by back titration of the EDTA excess. In the other aliquot of 100 ml the calcium is precipitated in slightly acetic acidic medium as oxalate and according to the procedure mentioned above the calcium is determined by direct titration using Erioblue SE indicator. There is an other possibility too: the calcium is precipitated according to the rapid method suggested by SAJÓ, the calcium oxalate precipitate is filtered off, then washed back into the beaker used for the precipitation. The bulk of the precipitate in the beaker and its traces on the filter are dissolved with hot dilute sulfuric acid and the solution is diluted to 200 ml with hot water and titrated with 0.1 N potassium permanganate solution. The data given in the proof analyses in Appendix are obtained by this method.

It is to be noted that under the given conditions also the barium, if present, remains in the resin bed like the calcium and magnesium and the three cations mentioned will be together eluted at pH 11. Further, determining the sum of calcium and magnesium by back titration of the EDTA excess in the effluent, really the sum of the three cations is determined. Moreover, it is to be mentioned that in the presence of barium accurate results can not be obtained at the direct titration of calcium against Erioblue SE indicator and the presence of barium also interferes if the calcium is precipitated as oxalate determining its amount permanganometrically. To solve the problem, the



following way seems to be possible: first is to be determined the sum of calcium, magnesium and barium by back titration of the EDTA excess in the effluent, then to precipitate the barium as sulfate from homogeneous solution and after filtration of the precipitate to determine the amount of the barium. The precipitation of calcium as oxalate may be carried out in the filtrate of barium sulfate, finally the filtered calcium oxalate is ignited, dissolved and its calcium content is determined by direct titration with EDTA against Erioblue SE. In this case the possible co-precipitated sulfate ions do not interfere the determination of calcium which would be the case if the calcium content should be permanganometrically determined. (Precipitating the calcium as oxalate from solutions containing also sulfate ions also calcium sulfate may be co-precipitated together with calcium oxalate; permanganometrically only the calcium content present as oxalate can be determined.) The investigations to find the most appropriate procedure for separation and determination in the presence of barium are in progress.

## APPENDIX

### 1. Solutions, buffers and indicators used

*0.05 M disodium EDTA solution:* 93.025 g disodium EDTA dried at 80°C is dissolved and diluted to 5000 ml with deionized water without adding sodium hydroxide. Standardize with 0.05 M magnesium chloride solution.

*0.05 M zinc acetate solution:* dissolve and dilute 54.86 g zinc acetate to 5000 ml. Before filling up to the mark acidify with a few ml of acetic acid. Standardize with the 0.05 M EDTA solution used.

*Acetate buffer of pH 4,7 :* 1 : 1 solution of N sodium acetate and N acetic acid.

*NH<sub>3</sub>—NH<sub>4</sub>Cl buffer of pH 10:* 70 g ammonium chloride is dissolved in 200 ml deionized water, then 570 ml ammonium hydroxide (sp. w. 0,91) is added and the solution is filled up to 1000 ml.

*0.05 M EDTA solution buffered to pH 11 according to FRIESE:* 15.46 g boric acid, 10 g sodium hydroxide and 18.61 g disodium EDTA is dissolved and filled up to 1000 ml. Standardize partly with 0.05 M magnesium chloride solution, partly the zinc acetate solution used is also to be standardized to this buffered EDTA solution.

*Sulfosalicylic acid indicator:* in aqueous solution of 10 per cent.

*Xylenol orange indicator:* it may be applied in aqueous solution, dissolving 0.1 g in 100 ml water, or finely powdered mixture of 0.1 g indicator and 100 g potassium nitrate is used.

*Erioblue SE indicator:* dissolve 0.1 g in 100 ml of water.

*Erioblack T indicator:* finely powdered mixture of 1 g indicator and 200 g sodium chloride.

### 2. Proof analyses

a) Solutions introduced into the ion exchange columns contain:

Fe	11.21 mg
Al	10.71 mg
Mn	15.32 mg.

Iron is determined only in aliquots taken from the stock solution.

After separation by ion exchanger in the effluents the following amounts of aluminum and manganese, respectively, were found:

mg Al		mg Mn	
	10.84		15.46
	10.84		15.46
	10.81		15.46
	10.81		15.46
	10.66		15.46
	10.70		15.46
	10.73		15.41
	10.70		15.46
<i>M</i>	10.76 mg Al	<i>M</i>	15.45 mg Mn
<i>s</i>	$\pm 0.0715$ mg	<i>s</i>	$\pm 0.0181$ mg
<i>s<sub>x</sub></i>	$\pm 0.0252$ mg	<i>s<sub>x</sub></i>	$\pm 0.0073$ mg
<i>C</i>	$0.66\%$	<i>C</i>	$0.11\%$
<i>E</i>	$0.235\%$	<i>E</i>	$0.047\%$

b) Solutions introduced into the ion exchange columns contain:

Fe	5.59 mg
Al	2.73 mg
Mn	30.61 mg.

Iron is determined only in aliquots taken from the stock solution.

After separation by ion exchanger the following amounts of aluminum and manganese, respectively, were found in the effluents:

mg Al		mg Mn	
2.63	2.63		30.65
2.66	2.67		30.46
2.63	2.74		30.68
2.78	2.78		30.54
2.74	2.63		30.65
2.75	2.74		30.73
2.73	2.71		30.76
2.74	2.74		30.40
2.76	2.76		30.38
<i>M</i>	2.71 mg Al		30.87
			30.46
		<i>M</i>	30.60 mg Mn
<i>s</i>	$\pm 0.053$ mg	<i>s</i>	$\pm 0.160$ mg
<i>s<sub>x</sub></i>	$\pm 0.012$ mg	<i>s<sub>x</sub></i>	$\pm 0.048$ mg
<i>C</i>	$1.95\%$	<i>C</i>	$0.52\%$
<i>E</i>	$0.46\%$	<i>E</i>	$0.15\%$

c) Solutions introduced into the ion exchange columns contain:

Fe	9.65 mg
Al	5.10 mg
Mn	4.09 mg
Ca	9.24 mg
Mg	4.74 mg.

Iron is determined only in aliquots taken from the stock solution.

After separation of the components mentioned by ion exchanger the following amounts of aluminum, manganese, calcium and magnesium, respectively, were found in the effluents:

	<u>mg Al</u>		<u>mg Mn</u>
	5.30		4.17
	5.12		4.17
	5.26		4.09
	5.28		4.09
	5.30		4.09
	5.31		4.17
	5.30		4.09
	5.28		4.09
<i>M</i>	5.26 mg Al	<i>M</i>	4.12 mg Mn
<i>s</i>	= ±0.0628 mg	<i>s</i>	= ±0.041 mg
<i>s<sub>x</sub></i>	= ± 0.0222 mg	<i>s<sub>x</sub></i>	= ±0.014 mg
<i>C</i>	= 1.19%	<i>C</i>	= 0.99%
<i>E</i>	= 0.42%	<i>E</i>	= 0.35%

	<u>mg Ca</u>		<u>mg Mg</u>
	9.10		4.58
	9.40		4.40
	9.35		4.58
	9.15		4.73
	9.55		4.48
	9.35		4.60
	9.40		4.57
<i>M</i>	9.32 mg Ca	<i>M</i>	4.56 mg Mg
<i>s</i>	= ±0.015 mg	<i>s</i>	= ±0.100 mg
<i>s<sub>x</sub></i>	= ±0.058 mg	<i>s<sub>x</sub></i>	= ±0.038 mg
<i>C</i>	= 1.60%	<i>C</i>	= 2.19%
<i>E</i>	= 0.60%	<i>E</i>	= 0.80%

The statistical terminology used in connection with the proof analyses is as follows:

*standard deviation*:  $s = \pm \sqrt{\frac{\sum d^2}{n-1}}$ , where *d* means the deviation of an observation from the mean *M* and *n* is the number of observations,

*standard error*:  $s_x = \frac{s}{\sqrt{n}}$

*relative deviation*:  $C = \frac{s}{M} \cdot 100,$

*relative error*:  $E = \frac{C}{\sqrt{n}}.$

Concerning the precision and accuracy in chemical analysis of silicate rocks see paper of FAIRBAIRN and co-workers [1951] as well as the paper of G. CSAJÁGHY [1959].

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