ANALYTICAL METHODS OF MANGANESE ORES II.

Contribution to the determination of zinc and titanium in manganese ores

by

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INTRODUCTION

In one of his earlier papers [GRASSELLY, 1961] dealing with rapid methods of analysis of manganese ores, the author proposed new method for the separation of the Fe—Al—Mn—Ca—Mg content, by ion exchange technique using the corresponding complexometric method for the determination of the single components.

Extending the rapid methods on further components, the present paper is dealing on the one hand, with the possible errors due to the presence of Ti and with the problem of the most purposeful determination of Ti in the analytical process developed earlier, on the other hand, with method of analysis of manganese oxides for zinc.

EXPERIMENTAL

According to the analytical process described in the paper reffered, the separation of Fe—Al—Mn—Ca—Mg is performed by using a cation exchanger Wofatit KPS—200 [Cl⁻]. To the aliquot parts of 50 ml — taken from 500 ml of stock solution prepared after the dissolution of 1 g of manganese ore — 0,05 M EDTA solution is added in excess about of 50 p. c. compared to the amount necessary for complexing the expected Fe+Al content of the aliquot. The solution is then adjusted by acetate buffer to pH 3,5; after boiling it is cooled down, let finally washed with 150 ml of water. Fe+Al will be present in the effluent, while the other components remain in the column, from where at proper pH value, they can be eluted and determined separately, using a given excess of 0,05 M EDTA. The pH value of the effluent is adjusted to 5,6 by means of hexamethylenetetramine, and the excess of 0,05 M EDTA is titrated back by 0,05 M solution of zinc acetate against xylenolorange indicator. Thus, we obtain the amount of 0,05 M EDTA equivalent to that of Fe+Al present. On the other hand, iron has already been titrated at pH 2—3 in a similar volume of stock solution, so that the quantity of Al can be given by the difference

of these two measurements. Here we are faced with the question as to how the above-outlined working process should be modified for additional two components, Zn and Ti, and how the determination of these two components could be fit in the most suitable way in the given set of analyses.

1. Determination of zinc

The various manganese oxides, such as chalcophanite $[ZnMn_3O_7 \cdot 3H_2O]$, franklinite $[(Zn,Mn,Fe)(Fe,Mn)_2O_4]$, woodruffite $[(Zn,Mn)_2 \cdot Mn_5O_{12} \cdot 4H_2O]$, hetaerolite or hydrotaerolite $[ZnMn_2 \cdot (O,OH)_4]$ or Zn-bearing todorokite, contain more or less zinc, too. In addition, the determination of zinc may also be of interest for the study of various ferrites.

If a solution contains, along with Fe—Al—Mn—Ca—Mg, some Zn too, then under the circumstances of the above method, zinc will get in the eff-luent solution, together with iron and aluminum. For instance, under the given circumstances 32,06 mg of Zn was introduced into the column and 31,95 mg of Zn was found in the effluent. Error equals 0,11 mg. Consequently, if the effluent contains some Zn, the available method of determination of Fe and/or Al can no longer be applied unreservedly, because Zn must either be masked or previously removed.

This latter seems to be the more suitable approach for the simple reason that the expected zinc content is as a rule smaller than that of Fe(Al) or especially that of Mn (unless explicitly Zn-bearing manganese ores, such as those mentioned previously, but manganese ores having Zn-bearing manga-nese oxide components too, are under consideration), so that the ion exchange technique used for the separation of zinc may serve as enrichment technique as well.

a) Possibilities of separating zinc
from other cations by using anion exchangers

In analysing ferrites DONALD H. WILKINS [1959] applies a strongly basic anion exchanger resin for the separation of zinc, cobalt, nickel, and iron. The Ni content of the solution (9 N for hydrochloric acid) passes through the anion exchanger column and can be washed out quantitatively with 9 N hydrochloric acid, whereas the chlorocomplexes of Co, Fe, and Zn will remain in the resin bed, from where they can be eluted, first the Co by 4 N hydrochloric acid, then the Fe by 0,5 N hydrochloric acid. Finally, Zn is eluted by 3 N nitric acid. The eluates are evaporated in order to remove the excess of acid. Thereafter, they are taken up by water and after adding of EDTA solution in excess the pH is adjusted to 4,8. The excess of EDTA is then titrated back by standard CuSO4 solution using PAN indicator. After the elution of zinc the column is rinsed by water, then regenerated by washing it with hydrochloric acid.

Similar experiments were run by D. JENTZSCH and I. FROTSCHER [1954]. They used anion exchanger Wofatit L—150 for the separation of cations. The method was similarly based upon the different adsorption properties of the chloro-complexes. The separation of the individual components was performed by means of elution on the column, using solutions with decreasing hydrochloric acid concentrations. The Ni introduced in 10 N hydrochloric acid, passes through the column, whereas Co remains in the column, from where it can be eluted by 6,5 N hydrochloric acid.

In his book PŘIBIL [1961] refers to the paper of A. M. AMIN and N. I. FARAH [1955]. According to this paper the zinc is separated also by anion exchanger in form of chloro-complexes from the other components. These authors propose to use anion exchanger Am-berlite IRA—400 treated previously with 2 N hydrochloric acid. Again, the solution is introduced into the top of the column in 2 N solution of hydrochloric acid. The zinc is retained in the bed from where it can be eluted by water and 0,025 N nitric acid.

4

As shown in the above discussion, under proper circumstances Zn can be separated in 2 N solution of hydrochloric acid already and one need not use 10 N or 9 N solutions of hydrochloric acid. This approach is so much the more advantageous, as on the one hand, after the weighed sample of manganese ore has been dissolved, zinc can be removed in this way by anion exchanger from each aliquot part of stock solution before the separation of Fe+Al+ +Mn+Ca+Mg. By evaporation of the effluent the excess of acid can be removed and the solution can be introduced into the cation exchanger in order to separate the other cations. On the other hand, the zinc eluted from the anion exchanger, can be quantitatively determined. However, if an extremely small quantity of zinc is only expected, it is useful to introduce all the solution obtained by dissolving the manganese ore sample into the anion exchanger, so that the whole zinc content of the sample will be enriched in the bed.

Now the following questions will only have to be answered: Under the given conditions (Amberlite IRA—400; grain size 0,2 mm ∅; inner diameter of resin column 10 mm; height of resin column 100 mm) and in presence of the cations taken into consideration, in solutions of hydrochloric acid of what normality does zinc remain quantitatively on the column? Under which circumstances can it be eluted? Is the separation of the other cations — such as Fe, Al, Mn, Ca, and Mg — from zinc perfect?

Sorption step

Using 2 N and (in another run) 0,5 N solutions of hydrochloric acid, aliquot parts of solution of known zinc content were introduced into the anion exchanger which, in turn, had been washed out previously with 2 N and 0,5 N hydrochloric acid, respectively. After the zinc-bearing solution passed through the resin column, the latter was washed with 5×20 ml of 2 N or (in the other run) 0,5 N hydrochloric acid. In the effluent solution zinc could not be determined, it remained quantitatively in the bed either 2 N or 0,5 N hydrochloric acid was used.

Elution step

We first attempted to perform the elution of zinc with water and 0,025 nitric acid, as described in the paper of AMIN and FARAH, but under the given circumstances the zinc could not be completely eluted from the column even when washed for a long time.

We found, however, another, more successful approach. After washing with 2 N or 0,5 N hydrochloric acid, the collected effluent and wash liquid is put aside (any cations other than zinc will be present in these solutions), the resin bed is washed first with 10 ml of water, then with 20 ml of ammonium-ammonium chloride buffer solution diluted 1:1 (which is used in complexometric titration against indicator Eriochromblack T for adjusting pH to 10) and finally with 3×10 ml of water, too. The amount of zinc is determined in this collected solutions titrated by 0,05 M EDTA against Eriochromblack T indicator. Under these conditions, the elution is perfect. The

amounts of zinc found in the eluates correspond well to those determined in the aliquot parts of stock solution, as illustrated in Table 1.

TABLE 1.

Amount of Zn in mg		Amount of Zn in mg	
Added	Determined	Added	Determined
in 2 N hydrochloric acid		in 0,5 N hydrochloric acid	
6,70	6,67	12,28	16,28
9,97	9,94	32,56	32,59
16,41	16,38	48,84	48,74
		80,74	80,84

Thereafter the regeneration of the column can follow by 2 N and 0,5 N hydrochloric acid, respectively.

As mentioned previously, an additional question was, whether the other cations present under similar circumstances would get into the effluent solution, or not, whilst the zinc is retained quantitatively in the bed.

Therefore, known quantities of the single cations were added separately into the anion exchanger, using 2 N solution of hydrochloric acid in the first run and 0,5 N in the second one. After the effluent solution has dropped, the bed is washed with 5×20 ml of 2 N and 0,5 N hydrochloric acid, respectively, the solution is evaporated and the amount of the cations is determined complexometrically. The data obtained in this way are shown in Table 2.

It follows from the above that the occasional zinc content of manganese ores can be separated from the other cations and then determined, as follows:

1. 50 ml aliquots (if greater amount of zinc are expected) of the stock solution prepared by dissolving the manganese ore sample (as described in the introductory paper quoted above) are evaporated, the residue is taken up by 0,5 N hydrochloric acid and the solution is let pass through an anion exchanger Amberlite IRA—400 treated formerly with 0,5 N hydrochloric acid. Then the column is washed with 5×20 ml of 0,5 N hydrochloric acid. Zinc remains in the bed, the other components being present in the effluent.

2. The collected effluent and wash liquid is evaporated in order to remove the excess of acid. Afterwards, the residue is taken up by water, 0,05 M EDTA is added in excess of known amount, the pH is adjusted to 3,5, and the solution is introduced into a cation exchanger Wofatit KPS—200 for separating the other cations (see the first paper).

3. The anion exchanger is washed first with 10 ml of water, then with 20 ml of ammonium-ammonium chloride buffer diluted 1:1, finally with 3×10 ml of water. The amount of zinc in the eluate (diluted to 100 ml) is titrated by 0,05 M EDTA solution using Erioblack T as indicator.

(If a low zinc content is expected, it is advisable to prepare the stock solution a priori, in such a way that it should be 0,5 N for hydrochloric acid, and the whole stock solution is let pass through the anion exchanger. This time the zinc content of the whole weighed sample will concentrate in the anion exchanger. The anion exchange bed washed

TABLE 2.

	Metals, in mg, added into the anion exchanger using			
	0,5 N hydrochloric acid		2 N hydrochloric acid	
	and determined in the effluent solution			
	Added	Determined	Added	Determined
Fe	27,42	27,31	27,73	27,73
		27,26		27,67
		27,17		27,65
		27,25		27,68
Al	13,29	13,35	13,17	13,22
		13,34		13,22
		13,33		13,22
		13,34		
Mn	27,11	27,08	27,39	27,25
		27,08		27,30
		27,08		27,36
				27,30
Ca	10,20	10,18	20,10	20,08
		10,16		20,12
		10,20		20,14
		10,18		20,11
Mg	6,08	6,14	12,18	12,18
		6,15		12,19
		6,13		12,18
		6,14		12,18

with 0,5 N hydrochloric acid and the effluent is evaporated for removing of the bulk of the excess of acid. Thereafter, the residue is taken up and poured into a 500 ml measuring flask and filled up to the mark. From this solution aliquots of 50 ml are introduced into a cation exchanger Wofatit KPS—200.)

2. Determination of titanium

The influence of the presence of Ti on the set of analyses is worth of consideration, because minimal amounts of Ti may be present in manganese ores, too, due to the admixture of accessory mineral components, and also because the analytical process developed for manganese ores can certainly be applied, mutatis mutandis, to silicate analyses as well.

The presence of titanium raises the following questions:

a) Does titanium, during the separation outlined in section 1, pass into the effluent solution, together with iron and aluminum?

b) Is in the presence of titanium that precision method applicable to back titration of excess of EDTA which proved good in presence of iron+auminum?

c) Which method can be used most advantageously for the determination of titanium?

7

a) *The influence of the presence of titanium on the analytical process*

The solution used in the experiments contained merely titanium (1 ml = $= 0,195$ mg TiO_2). In one set of analyses 0,05 M EDTA was given in known excess to aliquot parts of 10 and 25 ml, respectively, taken from the stock solution. Thereafter, the solution was adjusted to pH 5,6 by means of hexamethylenetetramine and the excess of EDTA was titrated back by 0,05 M zinc acetate solution against xylenolorange indicator, determining in this way the ml-s of EDTA equivalent with the titanium present. In the other set of analyses similarly 10 or 25 ml aliquots of Ti solution were taken and adjusted to pH 3,5 by acetate buffer. After the necessary excess of EDTA was added to the solution, it was let pass through a cation exchanger Wofatit KPS—200. As the excess of EDTA in the effluent solution was titrated back under the circumstances described above, the amount of titanium was similarly determined. The results are summarized in Table 3.

TABLE 3.

TiO_2 mg calculated	TiO_2 determined in aliquot parts of stock solution by back titration of the excess of EDTA mg	TiO_2 passed through ion exchanger, determined in effluent solution by titrating back the excess of EDTA mg
1,95 mg	1,87 mg 1,91 1,95 1,95 1,92 mg —0,03	1,96 mg 1,83 1,87 1,87 1,88 mg —0,07
4,87 mg	5,07 mg 5,03 4,95 4,95 5,00 mg +0,13	4,87 mg 4,87 5,03 4,97 4,93 mg +0,06

The above results show, on the one hand, that under the above circumstances the titanium content of the solution introduced into the cation exchanger Wofatit KPS—200 passes completely into the effluent together with iron and aluminum, on the other hand, that in the effluent the excess of EDTA can be readily titrated back by zinc acetate solution against xylenolorange indicator at pH 5,6, even if Ti is present. End point is just as sharp as in presence of iron+aluminum.

Consequently, titrating back the excess or EDTA in the effluent in presence of Fe+Ti+Al, one determines the quantity of EDTA equivalent to the sum of the three cations, and the method of analysis need not be modified because of the presence of Ti, at least as far as separation is concerned. The only difference is that we have to take into consideration, besides the expected amount of iron and aluminum, that of Ti as well, in order to assess approximately the amount of EDTA to be added to the solution for avoiding the use of an unnecessarily great excess:

b) Possibilities of the determination of titanium in the effluent

In his book Přibil [1961] refers to one of I. Sajo's papers [1954] according to which Fe+Ti+Al can be determined in such a way that first the amount of 0,05 M EDTA equivalent to that of Fe+Ti+Al is determined by titrating back the excess of EDTA of known quantity added to the aliquot part of solution and then 10 ml of 10% diammonium hydrophosphate solution (containing per liter 20 ml hydrochloric acid of 1,12 Sp.g.) is added to the solution. A few minutes later, titanium precipitates in form of titanium phosphate and an equivalent amount of EDTA is released. This latter is, in turn, titrated back by 0,05 M zinc acetate solution and the amount of titanium is thus determined. Thereafter, 30 ml of saturated, neutral NaF solution is added to the solution, so that an amount of EDTA equivalent to aluminum is released, which is also titrated back by zinc acetate, determining in this way the amount of aluminum. The author referred to above observed a fluctuation around 0,2 mg of the values obtained while determining aluminum.

The above method was first tested on Ti solution. In doing so, to the solution with known Ti content 0,05 M EDTA was added in excess which was titrated back (see results of titration in Table 3), then the required diammonium hydrophosphate solution was added to the former and a few minutes later the amount of EDTA released, equivalent to Ti content, was titrated. The results are shown in Table 4.

TABLE 4.

Amount of titanium (TiO_2 mg) as determined by titrating back the amount of 0,05 M EDTA released on adding ammonium phosphate after back titration of the excess of 0,05 M EDTA.

TiO_2 mg calc.	In aliquot parts of stock solution	In aliquot part of solution passed through exchanger
	1,95 mg	1,95 mg
	1,99	1,91
	1,95	1,87
1,95 mg	1,95	1,83
	1,96 mg +0,01	1,89 mg —0,06
	4,91 mg	4,83 mg
	4,83	4,91
	4,83	4,87
4,87 mg	4,87	4,79
	4,86 mg —0,01	4,85 mg —0,02

The above analyses certainly suggest that if ammonium phosphate is added, exact results can also be obtained by titrating back the amount of EDTA released from the Ti-EDTA complex. We wonder, however, if similarly reliable results can be obtained in cases when both titanium and aluminum are present. For this very reason, we added the necessary excess of EDTA to aliquot parts of stock solution containing known amounts of aluminum, afterwards, at pH 5,6, we titrated back the excess by 0,05 M zinc acetate solution against xylenolorange indicator, determining thereby the amount of aluminum (see Table 5, values *a*). Thereafter, 15 ml of 10% solution of diammonium hydrophosphate was added to the solutions. As shown by Table 5, with increasing aluminum content, increasing amounts of EDTA were released

although no titanium was present. In other words, it seems that if both titanium and aluminum are present, the separation of titanium by ammonium phosphate and by titrating back of the released EDTA is not altogether unambiguous — at least not under the present experimental conditions —, as some aluminum is also precipitated and an equivalent amount of EDTA is also released, which are both titrated back during the back titration of the released amount of EDTA equivalent to Ti. The values x in Table 5 give the amounts of aluminum precipitated at an increasing rate with increasing aluminum content. The next step is to add 30 ml of saturated NaF solution to the former. Aluminum precipitates then as cryolite. The amount of aluminum is determined by titrating back the released amount of EDTA. The results are represented by values y in Table 5. As shown by these data, they fall short of the values a determined for Al by back titration of excess of EDTA, whereas the sum of the values $x+y$ show a very good agreement with both the calculated amounts of aluminum and the values a (determined by back titration of excess of EDTA). The differences between the values obtained by back titration and those calculated are, except for a few measurements, less than 0,1 mg, whereas the measured amounts (y) of aluminum fall by 0,15—0,30 mg short of the calculated values even in presence of 10—20 mg Al. This stands to reason, since this lacking amount of aluminum precipitated as early as during the treatment by ammonium phosphate and the equivalent amount of EDTA had already been titrated back, which, in turn, caused a + error in the determination of Ti. Presumably, this is the reason for the fluctuation of values around 0,2 mg, a fact pointed out in I. Sajo's paper, too.

TABLE 5.

Al computed	a	x	y	$x+y$	$x+y/a$ $\varDelta$	$x+y$/comp. $\varDelta$
		Al	in mg			
1,348	1,36	0,08	1,26	1,34	—0,02	—0,008
2,696	2,64	0,09	2,57	2,66	+0,02	—0,039
6,740	6,75	0,15	6,59	6,74	—0,01	0,000
13,480	13,40	0,19	13,21	13,40	0,00	—0,080
20,220	20,24	0,28	19,89	20,17	—0,07	—0,050
1,348	1,35	0,05	1,27	1,32	—0,03	—0,028
2,696	2,67	0,05	2,63	2,68	+0,01	—0,016
6,740	6,71	0,09	6,58	6,67	—0,04	—0,070
13,480	13,42	0,15	13,25	13,40	—0,02	—0,080
20,220	20,22	0,20	19,98	20,18	—0,04	—0,040
1,348	1,35	0,12	1,21	1,33	—0,02	—0,018
2,696	2,64	0,09	2,69	2,78	+0,18	+0,084
6,740	6,72	0,16	6,55	6,71	—0,01	—0,030
13,480	13,41	0,21	13,13	13,34	—0,07	—0,140
20,220	20,30	0,29	19,87	20,18	—0,12	—0,040

The values x and y and their divergences from values a and from the values computed, as shown in Table 5, suggest that during separation by ammonium phosphate some aluminum also precipitates together with titanium, and therefore the amount of EDTA released this time is greater than would

correspond to the actual titanium content (a positive error in Ti determination), and that just as much less is the amount of aluminum determined by back titration after precipitation by NaF (a negative error in Al determination). The aforementioned error increases with increasing amount of aluminum, as illustrated by Fig. 1, too. In this figure, we plotted, on the ordinate, those values of 0,05 M EDTA which had been released (amounts épuivalent to aluminum separated) on treatment by ammonium phosphate, while on the absciss we plotted the ammounts of 0,05 EDTA released on subsequent treatment by NaF. The sum of the two values is equivalent to the actual amount of aluminum present.
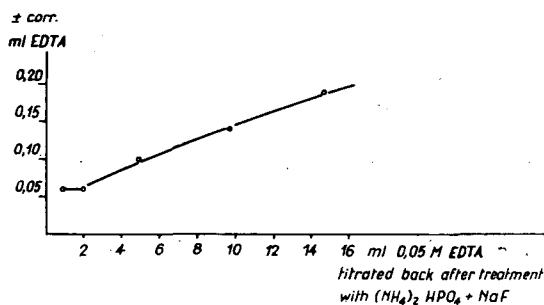
Error to be corrected in determining titanium and aluminum one after another

Considering the above, once Fe+Ti+Al (supplied into he effluent in the course of the applied set of analyses) are separated from the other cations, two possibilities offer themselves for determining separately the amount of iron, titanium, and aluminum.

The first one is that after the number of milliliters of 0,05 M EDTA equivalent to the total amount of the three cations present is determined by back titration of the excess of EDTA in the effluent, the excess is titrated back at pH 5,6 by 0,05 M solution of zinc acetate using xylenolorange indicator and to the solution 15 ml of 10% solution of diammonium hydrophosphate is added. After a few minutes of delay (pH being readjusted, if necessary, and some indicator added, again, to the solution), the amount of 0,05 M EDTA released is titrated. In presence of Al we take off therefrom the amount of correction dependent on the amount of Al, to be read off Fig. 1, so that the number of milliliters thus obtained will be equivalent to the amount of Ti present. Afterwards, 30 ml of saturated, neutral solution of NaF is added to the solution and the EDTA milliliters released are re-titrated at pH 5,6. The figure obtained being corrected as mentioned previously, we obtain the number of milliliters of 0,05 M EDTA equivalent to the actual amount of aluminum.

The second approach is that again the amount of 0,05 M EDTA corresponding to the total amount of Fe+Ti+Al is determined by back titration of the excess of EDTA in the effluent, but the effluent solution itself is not used for any further determinations. However, in the 50 ml aliquot taken from the original stock solution we determine, on the one hand, the iron content and the equivalent amount of 0,05 M EDTA, on the other hand, photometrically the amount of TiO₂ present and that of 0,05 M EDTA corresponding to it. Afterwards, these milliliter values are taken off, one by one, from those of

11

0,05 M EDTA determined earlier equivalent to the sum of .Ti+Al+Fe and the amount of aluminum is thus obtained.

These facts are so much the more worth of consideration, as the analytical process hitherto developed applies not only to manganese ores in which the presence of either iron, or titanium, or aluminum (particularly that of these latter two) is merely incidental due to admixture of various accessory minerals, but it can be used for the analysis of rocks as well. And, as regards these latter, here we always must reckon with aluminum and titanium contents higher than in the case of manganese ores. Still, the higher the aluminum content, the greater the error.

CONCLUSIONS

1. In the analysis of manganese ores the zinc content can well be separated from the other components, if the solution (0,5 N for HCl) is percolated through the anion exchanger Amberlite IRA—400 and if afterwards the column is washed with 0,5 N hydrochloric acid. The effluent will contain the other cations which can be separated from each other on cation exchanger Wofatit KPS- 200 by using the techniques developed earlier. Using ammonium-ammoniumchloride solution, zinc can be eluted from the anion ecxhanger and immediately titrated in the eluate. The column can be regenerated by 0,5 N hydrochloric acid.

2. *a)* The analytical process using ion exchangers developed for the separation of Fe-Al-Mn-Ca-Mg can be applied in presence of titanium, too, as Ti will completely pass into the effluent solution, together with iron and aluminum.

b) The sum of the amounts of iron + titanium + aluminum in the effluent can be exactly determined by back titration of the excess of EDTA, at pH 5,6, using zinc acetate solution against xylenolorange indicator.

c) The sum of iron + titanium + aluminum and the equivalent amount of 0,05 M EDTA, respectively, in the effluent being known, we can determine each of them successively. First Ti is determined by separating with ammonium phosphate and measuring the amount of EDTA released, then aluminum by separating with NaF and titrating the equivalent EDTA released according to I. SAJO's method, with the difference that titration is performed at pH 5,6 and xylenolorange is used as indicator. However, as shown by our measurements, in successive determinations increasing aluminum content is accompanied by increasing error. In fact, titanium contents greater and aluminum contents smaller than the actual amount are determined. At Al contents of 2—3 mg the error is still negligible, but in presence of 20 mg of Al it is as great as 0,3 mg. The use of corrections permits to eliminate the error and the results thus obtained are already satisfactory. The divergence of the corrected aluminum contents from the computed ones is -0,039 mg, in the mean.

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