ANALYTICAL METHODS OF MANGANESE ORES III.

Contribution to the determination of Na_2O and K_2O in manganese ores

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The determination of alkali content may be of interest and necessary, whether natural manganese ores or artificial oxides are studied. On the one hand, various natural manganese compounds may contain alkali metals, such as potassium contained in cryptomelane, but alkali metals as adsorbed cations may be contained in various manganoxihydrates, particularly in those precipitated in colloidal state. On the other hand, alkali, especially potassium, may be present in various artificial manganese dioxides in dependence on the production technique adopted.

In rapid methods of silicate analysis the alkali content is usually determined by flame-photometry. L. SHAPIRO and W. W. BRANNOCK [1956] determined the alkali metals without preliminary separation, using lithium sulphate as internal standard. J. P. RILEY [1958] removed the interfering Fe, Al, Ti ions by means of an anion exchanger Amberlite IRA—400 in its citrate form, where ammonium sulphate was added as buffer to both the sample solutions and the standard solutions. In the book of selected papers compiled by A. A. SMALES and L. R. WAGER [1960], E. A. VINCENT has proposed separation of interfering ions by ammonium hydroxide and ammonium carbonate. This method was applied by M. WEIBEL [1961], too, in his rapid process of rock analysis.

In view of the rather ample choice of methods available the only question we faced concerned the choice of the basic approach which would yield reliable results in a comparatively simple way in the analysis of manganese ores, i.e. in presence of considerable amounts of manganese.

EXPERIMENTAL

The determinations were carried out by means of Zeiss Flammenphotometer Modell III „A". Comparing the different methods for determination of Na_2O and K_2O, we found simple and, at the same time, reliable the method proposed by VINCENT and WEIBEL. Slightly modified (chiefly as far as the attacking and, in certain respect, the measuring techniques are concerned), it yields accurate results even at considerable manganese contents, as demonstrated by the analyses to be shown later in this paper.

I. Dissolution of the sample

1. 0,5 g of finely powdered manganese ore is weighed into a 250 ml beaker, 25 ml of 1:1 hydrochloric acid and a few drops of 30% hydrogen hyperoxide is added to the sample. The beaker is covered and slightly heated over a water bath. If after the cessation of effervescence some undissolved brownish-blackish grains are still visible at the bottom of the beaker, a few drops of hydrogen hyperoxide are added to the solution.

2. As the sample is completely dissolved and dark grains are no longer visible at the bottom of the beaker, the solution is brought to boil, and after a few minutes of boiling it is thoroughly washed into a platinum dish of suitable size, together with the possible insoluble residue. Afterwards, it is almost completely evaporated on a water bath.

3. 1 ml of 60% perchloric acid and 15 ml of 40% hydrofluoric acid is poured into the platinum dish (to dissolve the insoluble, silicate-bearing residue) and the hydrofluoric acid is expelled over a water bath. In case of considerable amounts of insoluble residue this latter operation is repeated by adding 15 ml of hydrofluoric acid.

4. After the removal of hydrofluoric acid the residue is moistened merely by perchloric acid. The platinum dish is put on a sand bath and most of perchloric acid is removed by careful heating. Once it is done, the dish is taken off from the sand bath, but do not allow to become completely dry.

5. After the second removal of perchloric acid, 1 ml of perchloric acid is poured into the platinum dish and some hot water is added to it, in order to dissolve the residue. Complete dissolution of the residue is achieved by washing thoroughly the contents of the platinum dish into a 100 ml beaker repeating this operation several times, taking care that the volume of the solution should not exceed 60—70 ml. The solution is then boiled for a short time.

6. After cooling the solution is transferred into a 100-ml graduated flask and filled up to the mark with ion-free water.

The alkali content is determined in aliquot parts taken from this solution by flame photometry. The volume of the aliquot parts taken depends on the alkali content to be expected.

II. Reagents and solutions

1. Stock solutions

A. Stock solution of NaCl: 0,9430 g of NaCl dried at 105 °C and 0,7920 g of KCl dried at 105 °C are weighed. Having been dissolved, they are poured into a calibrated 1000 ml measuring flask filled up to the mark with ion-free water: 1 ml of solution$=0,5$ mg $Na_2O+0,5$ mg K_2O. The solution is stored in a plastic vessel.

B. Ammoniacal-ammonium carbonate solution: 2 g of ammonium carbonate is dissolved in 100 ml of ammonium hydroxide diluted 1 : 9. Each time a fresh solution has to be prepared.

C. Blank test solution.

C_1. Concentrated: 1 ml of perchloric acid is poured into a 100 ml measuring flask and diluted by ion-free water up to the mark.

C₂. Diluted: 10 ml of concentrated blank test solution (C_1) (=0,1 ml of perchloric acid) is brought into a 100 ml measuring flask, diluted by water to 50—60 ml, added to it 5 ml of ammoniacal ammonium carbonate solution (B) and filled up with ion-free water up to the mark.

2. Preparation of the standard solutions

a) 1, 2, 4, 6, 8, 10 ml volumes of stock solution *A* are successively introduced into 100 ml graduated flasks (0,5, 1, 2, 3, 4, 5 mg Na_2O and K_2O, respectively).

b) 10 ml of concentrated blank test solution (C_1) is poured into each flask, being diluted to 50—60 ml.

c) The flasks are charged with 5 ml of ammonia-ammonium carbonate solution each, shaken up, and filled up to the mark with ion-free water. Afterwards, they are thoroughly shaken up once more, and the solution with precipitate is poured over into a plastic bottle (dry) provided with a well-sealing cover, where it is let stay for one day.

III. Determination of Na_2O and K_2O

1. Volumes corresponding to the alkali content expected are taken with a pipette or burette from 100-ml sample stock solution obtained following the attack, and each is poured into a 100 ml measuring flask.

Since in the above standard Na+K solution series the extreme values of the alkali concentration are 0,5 mg/100 ml and 5,00 mg/100 ml Na_2O or K_2O, respectively, it is advisable to take such aliquot parts from the stock solution that their alkali content should fall within these two limits.

2. To the aliquot parts of stock solution poured into the flask and filled up to 50—60 ml with water add 5 ml of ammoniacal ammonium carbonate solution, mixed well, and filled up to the mark with ion-free water, then after repeated mixing the solution with the precipitate is poured over into a dry plastic bottle provided with a well-sealing cover, where it is let stay for one day, just as was the case with the standard solutions.

3. Using Na filter, the members of the standard solution and afterwards the sample solutions are atomized, one by one, into the flame. The atomization of the standard solutions and of the sample solutions is repeated alternately at least three times. In the further course of the analytical process the mean values of galvanometer readings are taken and then plotted.

After the atomization of the individual samples it is the diluted blank test solution (C_2) that will be atomized and the values of the corresponding readings are discounted from those of both the calibrational series and the samples analysed.

From the plastic bottle the clear solution above the precipitate is atomized. The precipitate itself need not be filtrated previously, we must merely take care that the precipitate should not be stirred up to avoid precipitate particles entering the atomizer.

4. After the determination of Na_2O, filter K is introduced and the K_2O content is determined in just the same way as previously and galvanometer readings proportional to K concentrations are taken.

5. The readings obtained for the members of the standard series are plotted in form of a calibration curve. Superimposing on the latter the galvanometer readings of the individual samples, we can determine the Na_2O and/or K_2O content.

IV. Precision and accuracy of determination

Following the above-outlined working process, we made first parallel determinations of the alkali content of a granite sample, then having attacked the same rock sample in one and the same way and having prepared the stock solution, we added different amounts of manganese to the solution to be atomized, before filling it up, and we performed the determination of the alkali content of this solution, too. The results are shown in Table 1.

TABLE 1.

Na_2O and K_2O contents of a standard rock sample as obtained by parallel measurements of the original sample and as determined in presence of different amounts of manganese

Na_2O % as determined					K_2O % as determined					Mn added mg/100 ml
in the original sample		in the same, but in presence of Mn			in the original sample		in the same, but in presence of Mn			
4,00	3,98	4,00	3,84	3,90	3,40	3,56	3,54	3,51	3,38	0,53
4,00	3,82	4,00	3,84	3,90	3,40	3,52	3,54	3,52	3,45	1,07
3,99	4,17	4,00	3,84	3,92	3,40	3,48	3,52	3,51	3,40	2,14
3,99	3,82	4,00	3,84	3,90	3,40	3,47	3,52	3,55	3,45	5,35
3,92	3,90	4,00	3,82	3,89	3,40	3,40	3,50	3,52	3,46	10,71
3,92		3,98	3,79	3,86	3,40		3,60	3,55	3,45	21,42
3,98		3,98	3,80	3,85	3,56		3,60	3,48	3,45	42,84
$x=3,95^0/_0$		$x=3,90^0/_0$			$x=3,44^0/_0$		$x=3,50^0/_0$			
$s=\pm0,0822$		$s=\pm0,0743$			$s=\pm0,0666$		$s=\pm0,0567$			
$s_{\bar{x}}=0,0237$		$s_{\bar{x}}=0,0162$			$s_{\bar{x}}=0,0164$		$s_{\bar{x}}=0,0123$			
$C=2,08$		$C=1,90$			$C=1,93$		$C=1,62$			
$E=0,60$		$E=0,41$			$E=0,559$		$E=0,353$			

The terminology of the parameters characterizing the accuracy of determination is the same as that applied in the author's first paper on manganese ore analysis [GRASSELLY, 1962], viz.: $x=$ mean; $s=$ standard deviation; $s_{\bar{x}}=$ standard error; $C=$ relative deviation, and $E=$ relative error.

In one of their paper FAIRBAIRN et al. [1951] have dealt with the precision and accuracy of different methods of rock analysis, relying on analyses from various laboratories. A similar comparative study of 16 parallel silicate analyses is reported by G. CSAJÁGHY [1959]. Here we have used only the data concerning alkali content in the references quoted. A comparison of FAIRBAIRN's and CSAJÁGHY's data concerning the accuracy of alkali determinations to those obtained by us in presence of considerable amounts of manganese indicates that the present analytical process provides reliable, accurate results even at high manganese contents and that it can certainly be applied successfully for the determination of the alkali content of manganese ores.

Precision of the determination of Na₂O and K₂O

	In rocks				In rocks in presence of manganese	
	as checked by the data of					
	FAIRBAIRN	CSAJÁGHY			the author	
	Na₂O	Na₂O	K₂O	K₂O	Na₂O	K₂O
x	3,26	5,51	3,21	4,42	3,90	3,50
s	0,284	0,549	0,173	0,218	0,082	0,056
$s\bar{x}$	0,06	0,11	0,043	0,054	0,016	0,012
C	8,71	9,96	5,39	4,93	1,90	1,62
E	1,81	2,07	1,35	1,23	0,41	0,35

CONCLUSIONS

Manganese ores can be advantageously analysed for Na₂O and K₂O by using, with slight modification, the method proposed by VINCENT and WEIBEL which essentially consists in separating the interfering ions by ammoniacal ammonium carbonate solution and determining subsequently the alkali content by flame photometry directly from the solution without filtering the precipitate. The manganese ores (either oxides or carbonates) are dissolved by hydrochloric acid adding to it a few drops of hydrogen hyperoxide or, provided some insoluble silicate residue is present, the attack by hydrochloric acid is followed by an attack by hydrofluoric acid — perchloric acid. The present analytical process yields accurate results even in presence of considerable amounts of manganese. And since the determination of the alkali content does not require to remove the disturbing ions by means of exchangers or to filter the precipitate, it can be performed in a simple way and relatively quickly, if only the actually necessary operations are considered (in fact, the precipitate is let stay for a night). In case of serial measurements, on one day the dissolution of the samples and the preparation of the solutions are performed, and on the following day we may proceed to measure the alkali content of the solutions prepared the day before.

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