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Determination of Chromium and Other Metal Oxides in Chromite Ores

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A study has been carried out on the separation of silica, iron, titanium, aluminium in chromite samples and their quantitative determination using conventional as well as with atomic absorption spectrophotometry. The dissolution conditions of the minerals with $HClO_4$ was optimized and compared with the fusion of the chromite ore with Na_2O_2. Perchloric acid dissolution was carried out on the reference standard samples and several chromite ores from Tamil Nadu. The recovery yields of individual metal oxides present in the mineral was found to be better than the Na_2O_2 fusion procedure. Good precisions were obtained for all samples and standards. The method is simple, rapid and economic and found to be ideal for the determination of iron, titanium, aluminium and silica in chromite rocks.

Key Words: Chromite, Metal oxides, Acid digestion.

INTRODUCTION

Chromite is the main chromium bearing mineral of commercial importance. It is known that chromite ores are very difficult to undergo whole rock analysis compared to the normal rock/clay samples. Determination of iron, titanium, aluminium and silica in chromite ores using inductively coupled plasma-atomic emission spectrometry (ICP-AES), ICP-MS, graphite furnace-AAS and neutron activation analysis have been reported[1]. But the difficulty in chromite ore analysis is the digestion of the ore. Manganese dioxide as an oxidizing agent with H_2SO_4 is used to dissolve the chromite ore[2,3]. A fusion procedure[4] with Na_2O_2 with NaOH is frequently applied to attack ores containing chromium. For the dissolution of such ores, recently microwave digestion system[5] has also been used.

In the present study, the dissolution of chromite ore is carried out using perchloric acid digestion. Silica is separated with Na_2CO_3 fusion and the solution is then analysed for metal oxides present in the ore by using

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both conventional as well as AAS. The results are in good agreement and it has been found that in the present ore analysis, there is not much chemical/ spectral interference. Na_2O_2 with NaOH fusion procedure was also carried out for these chromite samples and the results are compared with $HClO_4$ attack.

EXPERIMENTAL

A GBC-902 atomic absorption spectrophotometer (GBC scientific equipment) was used for the determination of chromium and other metal oxides. All reagents used are of analytical reagent grade.

Mixed 30 mL of $HClO_4$ with 0.5 g of chromium ore sample and digested at low heating over a hot plate for 3 to 4 h. When most of the black particle disappear, increase the heat till copious fume stops. If in case black particles of undecomposed chromite persist, dilute with water, decant off the supernatant solution into a 250 mL beaker and retreat the remaining black particles with 10 to 15 mL of perchloric acid. Care should be taken that the complete decomposition should not take more than 6 h. Black particles must fully disappear but undissolved silica particle may remain in the solution. This solution is mixed with the previous supernatant solution and 20 mL of dilute HCl is added and digested. The solution turns green after 10 to 15 min, filter through whatman filter paper carefully transferring the residue. Hot water washings must be given for several times until it is free of chlorides (solution 1). The residue is taken, ignited at 900 ºC, cooled and 3 to 4 g of sodium carbonate is added, mixed thoroughly with the help of a glass rod and fused at 1000 ºC in a muffle furnace. Leach the melt in 1:1 HCl and digested for 1 h and then the solution is allowed to bake to dryness[6]. The dried mass is again digested in 6 M HCl and filtered through Whatmann 42 filter paper into a 250 mL standard flask. The residue is weighed as silica. The above filtrate is mixed with the solution (1) and made upto 250 mL with distilled water (main solution).

R_2O_3[7]: 50 mL aliquot is taken from the main solution and a few drops of conc. HNO_3 and 2 to 3 g of NH_4Cl are added and boiled gently and then cooled to room temperature. Liquid ammonia is added in drops until the solution turns alkaline. Excess NH_3 present in the solution is boiled off and the solution is filtered through Whatmann 41 filter paper. Hot water washing must be given thoroughly. The filtrate (a) is collected in a 250 mL standard flask. The residue is dried in an air oven for 0.5 h at 105 ºC and then kept in a muffle furnace for 1 h at 1000 ºC, cooled and weighed.

Fe_2O_3: In order to determine Fe_2O_3, the procedure given under R_2O_3 may be followed by taking 100 mL of the main solution upto the filtration stage. The precipitate in the filter paper is dissolved with hot dilute HCl into a beaker; sufficient hot water washing may be given so as to fully dissolve the last traces of precipitate. Neutralize with 5 to 10mL of saturated NaOH (care must be taken to avoid the precipitation of sodium aluminate at this stage which may mislead the result). 5 to 7 g of Na_2O_2 is added with continuous stirring, keeping the beaker in a water bath. After the reaction subsides, the beaker is kept on a hot plate and boil till the oxygen evolution ceases. The contents of the beaker is filtered through whatman 41 filter paper with thorough hot water washings and the filtrates (1) are collected in a beaker and kept aside for Al_2O_3 determination. The precipitate is dissolved in hot 1:1 HCl with hot water washing into a conical flask. 10 to 15 mL of conc. HCl is added. The solution is boiled and the ferric ion is reduced by the addition of 6 % $SnCl_2$ solution. The solution turns colourless, cool under the running water and add 30 mL of acid mixture and 10 mL of $HgCl_2$ solution, silky white precipitate appears. 3 to 4 Drops of barium diphenylamine sulphonate indicator is added and the solution is titrated against $K_2Cr_2O_7$ and from the result, Fe is determined.

Al_2O_3: 5-7 g of Ammonium nitrate is added to the filtrate (1) with constant stirring and kept aside for ½ an hour. Then filter through whatman 41 filter paper with sufficient hot water washing, precipitate is ignited at 1000ºC for 1 h, cooled and weighed for alumina.

Cr_2O_3: 0.1 g of chromite ore sample is taken in a beaker and 30 mL of $HClO_4$ is added and kept over hot plate for digestion (keeping the beaker closed with watch glass). After all the chromium had gone into the solution, the solution turns orange in colour. Care must be taken that all the black particles have gone into the solution. The sides of the beaker is washed with distilled water, sufficient quantity of 0.1 N ferrous ammonium sulphate (about 25 to 50 mL) is pipetted and added to the solution and the excess FAS is titrated against 0.1 N $KMnO_4$. A blank determination of FAS against $KMnO_4$ is also conducted.

$$Cr_2O_3\% = \frac{(V1 - V2) \times 2.5345 \times \text{Strength of } KMnO_4}{\text{Sample weight}}$$

V1 - blank titre value; V2 - sample Titre value.

RESULTS AND DISCUSSION

The quantitative determination of the metal oxides in the chromite ore was found to be satisfactory by the proposed method. The efficiency of the $HClO_4$ digestion technique is very much comparable with that of Na_2O_2 digestion procedure and even the recovery of metal oxides in the proposed method is found to be much better for chromite samples containing about 30 % and less than 30 % of chromium content. The results obtained using Na_2O_2 fusion method and the proposed method are presented in Table-1

TABLE-1
COMPARISON OF RESULTS OBTAINED USING Na_2O_2 FUSION TECHNIQUE AND THE PROPOSED METHOD

	SiO_2			Cr_2O_3		
	C.V.	Na_2O_2	P.M.	C.V.	Na_2O_2	P.M.
RS1	7.55	7.41	7.61	27.75	27.68	28.40
RS2	13.70	13.02	13.62	21.80	20.78	21.99
RS3	11.15	10.16	10.96	24.20	23.56	24.46
RS4	15.10	14.76	15.21	30.35	30.42	30.33
S1	–	12.98	12.64	–	21.58	22.07
S2	–	13.71	13.70	–	22.65	23.09
S3	–	8.42	8.61	–	27.60	28.20
S4	–	14.82	14.26	–	30.58	31.36
S5	–	11.82	12.62	–	19.16	19.98
S6	–	9.18	9.97	–	24.78	25.46
	Fe_2O_3			Al_2O_3		
	C.V.	Na_2O_2	P.M.	C.V.	Na_2O_2	P.M.
RS1	27.60	27.02	27.74	20.15	19.90	20.24
RS2	30.90	30.15	30.82	20.55	20.10	20.63
RS3	32.76	32.35	32.65	20.46	19.85	20.52
RS4	17.80	17.41	17.95	21.46	20.88	21.68
S1	–	21.82	22.69	–	20.72	20.61
S2	–	26.82	27.59	–	19.59	19.43
S3	–	28.20	28.78	–	19.46	19.98
S4	–	16.68	17.20	–	21.18	21.70
S5	–	31.98	32.81	–	20.88	21.64
S6	–	32.15	32.85	–	20.76	21.56

RS= Reference standard; C.V.= Certified value; S= Samples (Chromite ores)

and the results are found to be in agreement with that of the certified values of the reference standard samples. 8 Individual metal oxides determination for the reference standard and the samples were performed to evaluate the reproducibility of the method followed. Good precisions were obtained for all samples and standard (Table-2).

It is known[6] that hot concentrated perchloric acid rapidly oxidizes metallic chromium and several of its compounds. In aqueous medium, perchloric acid releases chloride ions which attacks the chromium in geochemical soil samples. Chromium complexes with chloride ions and goes into the solution and hence the interference from silica in the determination is removed. At this stage, silica and other metal oxides will be present in the combined state. In order to separate out silica, the residue is fused with sodium carbonate, baked, digested and hence separated. Now the remaining metal oxides will be in the solution and their individual

TABLE-2
REPRODUCIBILITY OF VALUES OBTAINED BY THE PROPOSED METHOD

S. No.	R1	S1	S2	S3
1(Al_2O_3)	20.63	20.61	19.43	19.98
2	20.88	20.42	19.72	19.72
3	20.28	20.26	19.48	19.34
4	20.48	20.58	19.20	19.88
5	20.62	20.83	19.92	19.62
6	20.46	20.52	19.28	19.78
7	20.52	20.48	19.42	19.48
8	20.72	20.64	19.48	20.46
Mean	20.57	20.54	19.49	19.78
S.D	0.18	0.17	0.23	0.34
1(SiO_2)	13.62	12.64	13.70	8.61
2	13.92	12.80	13.89	8.65
3	13.55	12.35	13.32	8.20
4	13.24	12.59	13.69	8.85
5	13.82	12.35	13.42	8.55
6	13.75	12.90	13.90	8.32
7	12.98	12.31	13.58	8.45
8	13.18	12.25	13.79	8.75
Mean	13.63	12.52	13.66	8.55
S.D.	0.30	0.24	0.21	0.22
1(Cr_2O_3)	21.99	22.07	28.20	23.09
2	21.68	21.68	28.60	23.58
3	21.47	22.18	27.98	22.84
4	22.24	22.49	27.86	22.76
5	22.12	21.97	28.42	23.42
6	21.72	21.78	28.58	23.36
7	21.59	22.42	27.89	23.51
8	22.42	22.38	27.92	22.68
Mean	21.90	21.12	28.18	23.16
S.D.	0.34	0.30	0.31	0.36
1(Fe_2O_3)	31.81	22.69	27.59	28.28
2	31.68	22.10	27.88	29.12
3	30.92	22.48	27.18	29.72
4	30.88	22.62	27.48	28.48
5	31.42	22.82	28.10	28.82
6	32.21	22.46	27.28	28.86
7	31.57	22.52	27.52	28.63
8	31.82	22.64	27.34	28.75
Mean	31.54	22.54	27.55	28.83
S.D.	0.46	0.21	0.31	0.44

R = Reference standard; S = Samples (Chromite ores).

quantitative determination may be performed either by following conventional method or by atomic absorption spectrophotometry. In both the techniques, the results are found to be in good agreement.

An experiment on the optimization of the percentage recovery of chromium from the geochemical sample using perchloric acid is carried out and it has been found that the optimum recovery of chromium is achieved at 30 mL of perchloric acid (Fig. 1). In the present study, it has been found that the perchloric acid attack is very much suitable for those geochemical samples containing about 30 % and less than 30 % of chromium content than sodium peroxide fusion technique[1].

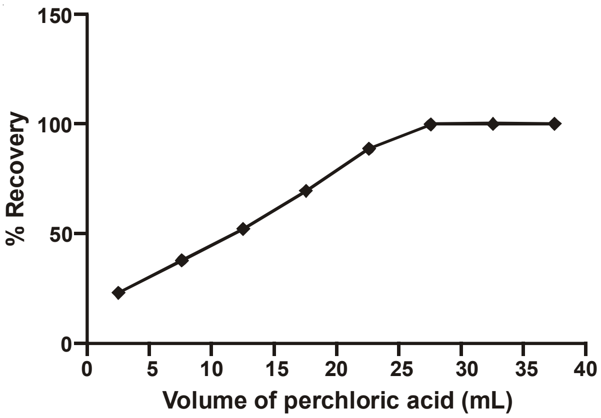

Fig. 1. Percentage of recovery of chromium

Taking the analytical accuracy of the proposed method into account, it is clear that almost all chromium and other metal oxides are recovered and estimated in the reference standards and in the chromite ore samples and hence the method is found to be consistent for the silicate analysis of chromite ore.

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