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CANADA

DEPARTMENT OF MINES AND TECHNICAL SURVEYS

OTTAWA

MINES BRANCH INVESTIGATION REPORT IR 62-62

**THE DETERMINATION OF METALLICS
IN FUSED CHROMITE ORE**

by

LEONARD G. RIPLEY

MINERAL SCIENCES DIVISION

NOTE: THIS REPORT RELATES ESSENTIALLY TO THE SAMPLES AS RECEIVED. THE REPORT AND ANY CORRESPONDENCE CONNECTED THEREWITH SHALL NOT BE USED IN FULL OR IN PART AS PUBLICITY OR ADVERTISING MATTER.

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Mines Branch Investigation Report IR 62-62

THE DETERMINATION OF METALLICS
IN FUSED CHROMITE ORE

by

Leonard G. Ripley*

- - -

SUMMARY OF RESULTS

The metallic phase of fused chromite ore can be separated from the chromite matrix by a selective solution procedure that uses iodine in anhydrous methanol as the solvent.

The variables in this isolation procedure have been investigated and are recorded.

The composition of the metallic phase has been determined by semi-quantitative spectrographic analysis and chemical-analytical methods.

*Senior Scientific Officer, Analytical Chemistry Subdivision, Mineral Sciences Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

CONTENTS

	<u>Page</u>
Summary of Results	i
Introduction	1
Identification of the Samples	2
Experimental-Analytical Procedures	2
1. Determination of Total Metallics	2
2. Determination of Metallic Iron	3
3. Determination of Metallic Nickel.....	3
4. Determination of Metallic Chromium.....	3
5. Determination of Metallic Silicon	3
6. Determination of Metallic Aluminum	3
7. Determination of Metallic Calcium	4
8. Determination of Metallic Magnesium	4
9. Determination of Metallic Copper	4
10. Determination of Total Carbon in Fused Chromite Ore ..	4
11. Determination of Total Graphite in Fused Chromite Ore.....	4
Results and Discussion	5
1. Variables in the Iodine-Methanol Method.....	5
(a) Time of Refluxing	5
(b) Weight of Sample	6
2. Composition of the Metallic Phase	6
3. Solubility of Carbides and Graphite in Iodine-Methanol Reagent.....	11
4. Conclusions	11
Acknowledgements	12
Appendix	13

INTRODUCTION

Seventeen samples of fused chromite ore were submitted for determination of metallic content by the Extraction Metallurgy Division, Mines Branch, Ottawa. These samples originated from a project being conducted by them for Canadian Refractories Limited.

The iodine-methanol reagent has been used successfully in the selective solution of metallics from the non-metallic components in mineral and metallurgical samples at the Mines Branch Laboratories, Ottawa.

The basic procedure involves the refluxing of a sample with a solution of iodine dissolved in anhydrous methanol. After several hours of refluxing, the reaction solution is cooled and filtered on a tared asbestos Gooch. The filtrate contains the metallics in the form of iodides; whereas, the non-metallics are collected on the Gooch. Analysis of these two phases can be made using standard methods.

When the tentative procedure was released to Mr. H. Booth, Canadian Refractories Limited, in a letter* dated March 13, 1962, it was stated a seventeen hour period of refluxing was employed; however, it was stated that this time interval was convenient but not specific.

The purpose of this report is to describe this new application of the iodine-methanol reagent for the removal of metallics from fused chromite ore samples.

* Correspondence relative to this investigation is included in the Appendix.

IDENTIFICATION OF THE SAMPLES

<u>Mines Branch Lab. No.</u>		<u>Identification</u>
315	P61-11-1	Head sample
1193	P61-11-2	Head sample
1895	P61-11-1	Top of button
1896	P61-11-1	Middle of button
1897	P61-11-1	Bottom of button
1898	P61-11-3	Tap 1 and Tap 2 composite
1899	P61-11-3	Head sample of fused button
1992	P61-11-1	BN magnetic fused
1993	P61-11-2	BN magnetic fused
1994	P61-11-3	BN magnetic fused tapped
1995	P61-11-3	BN magnetic fused from button
1996	P61-11-1	BN non-magnetic fused
1997	P61-11-3	BN non-magnetic fused from button
1998	P61-11-2	BN non-magnetic fused
1999	P61-11-3	BN non-magnetic fused
3027	P61-11-4	Sintered chrome ore
3028	P61-11-4	Fused chrome ore

The Mines Branch Laboratory number will be used for reference to these samples in the tables of this report.

EXPERIMENTAL-ANALYTICAL PROCEDURES

The samples were analysed as received.

1. Determination of Total Metallics

The metallic portion of the fused chromite ore samples was isolated by the following basic procedure:

A one gram sample is refluxed for several hours in an all glass apparatus with ten grams of iodine and one hundred* millilitres of anhydrous methanol. After cooling, the solution is filtered on a dried, tared asbestos Gooch. The residue is washed well with anhydrous methanol, dried at 100°C, cooled in a desiccator, and weighed. (The percentage of the sample that is soluble, i.e., the metallics, is readily calculated).

*The quantity of alcohol can be varied within \pm 25 ml without affecting the results.

The composition of the metallic phase was determined by evaporating the iodine and methanol from the above filtrate and analysing the non-volatile residue either spectrographically or by chemical procedures. In the latter case, the non-volatile residue was fumed into solution with perchloric acid. This resulting acid solution was used, either directly for specific determinations, or was made up to a definite volume and aliquotted for various analyses.

2. Determination of Metallic Iron

The iron in the acid medium was precipitated with ammonium hydroxide in the presence of ammonium chloride, filtered and washed with warm 3% ammonium chloride. The precipitate was then dissolved in hot 50% hydrochloric acid, the iron chloride reduced with stannous chloride and titrated with N/10 potassium dichromate.

3. Determination of Metallic Nickel

The filtrate from a double precipitation of the iron (see 2) was made up to 500 millilitres. The nickel was then determined spectrophotometrically with dimethylglyoxime in ten ml aliquots.

4. Determination of Metallic Chromium

The chromium, which was oxidized by fuming with perchloric acid, was titrated directly in a diluted solution with N/40 ferrous ammonium sulphate. The end-point was determined either electrometrically by an automatic titrator, or visually with diphenylamine indicator.

5. Determination of Metallic Silicon

The silicon in the non-volatile residue was dehydrated by the fuming perchloric acid. After filtration and suitable washing, the precipitate was ignited and the silica was determined by the hydrogen fluoride volatilization method.

6. Determination of Metallic Aluminum

The residue from the silica volatilization was fused with sodium bisulphate and added to the filtrate in the silica method. This filtrate was treated with $\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$ to remove the R_2O_3 group that was dissolved in dilute hydrochloric acid. The iron was removed by a chloroform extraction of the iron-cupferride. Aluminum was then determined by the usual NH_4OH precipitation and ignition to the oxide.

7. Determination of Metallic Calcium

The filtrates from the R_2O_3 and aluminum precipitations were combined and treated with ammonium oxalate. The calcium, which was precipitated as the oxalate, was determined by a potassium permanganate titration of oxalate equivalent.

8. Determination of Metallic Magnesium

The filtrate from 7 was treated with diammonium phosphate to precipitate the magnesium and manganese that were subsequently ignited to the pyrophosphates. The manganese content can be determined by the periodate colorimetric method and the magnesium content can be found by difference.

9. Determination of Metallic Copper

A suitable aliquot of the perchloric acid solution was treated with cuproine reagent and the copper was determined spectrophotometrically.

10. Determination of Total Carbon in Fused Chromite Ore

A one gram sample of chromite ore, mixed with tin and pure iron in a combustion boat, was burned in a stream of oxygen in a globar furnace at 2400°F. The carbon dioxide produced was trapped in ascarite and weighed.

11. Determination of Total Graphite in Fused Chromite Ore

Carbides were leached from the fused chromite ore with dilute nitric acid and the graphite was collected by filtration onto pre-ignited asbestos, dried, and ignited in oxygen in a combustion furnace. The liberated carbon dioxide was trapped in ascarite and weighed.

RESULTS AND DISCUSSION

1. Variables in the Iodine-Methanol Method

(a) Time of Refluxing

The refluxing time for three samples has been varied from two to seventeen hours. The results are shown in Table 1.

TABLE 1

Variation of Refluxing Time

Time (hrs)	Per cent Metallic		
	No. 1896	No. 1993	No. 3027
2	8.70	24.48	1.06
3	8.41	24.39	1.25
4	8.23	26.89	1.18
5	7.76	24.05	1.33
6	7.46	24.44	1.17
7	8.50	24.25	--
17	9.95	25.89	1.00
17	6.93	25.10	0.80
17	8.02	25.70	1.14
17	9.50	25.44	--
17	8.60	24.34	--
Average	8.37 [±] 0.62	24.99 [±] 0.73	1.12 [±] 0.12

It is apparent that the metallic phase has dissolved after two hours of refluxing and no further change occurs on longer heating.

The above conclusion is supported by X-ray diffraction analysis of the non-metallics obtained from No. 1898, which showed only one compound present, namely: $(\text{MgFe})\text{O} \cdot \text{Al}(\text{CrFe})\text{O}_3$ (where the ratio of Al to Cr plus Fe is 1:1).

(b) Weight of Sample

Ten grams of iodine combines with 2.2 grams of metallic iron; therefore, the iodine in the procedure is present in excess of the requirement for the iodination of the metallics in one gram samples of fused chromite ore. However, in order to determine whether or not the ratio of sample to iodine was a factor, various weights of No. 1993* were treated with ten grams of iodine in seventy-five millilitres of methanol. The results are in Table 2.

TABLE 2

Effect of Sample Weight in the Iodine-Methanol Method

Weight of Sample (g)	% Metallics
0.5	25.63
1.0	24.99
1.5	24.66
2.0	25.58

It is apparent that ten grams of iodine is sufficient for one gram samples of fused chromite ore.

2. Composition of the Metallic Phase

A semi-quantitative spectrographic analysis of the metallic phase indicated the following elements:

* This sample was chosen because it contains the greatest amount of metallics of the seventeen samples received.

TABLE 3

Semi-quantitative Spectrographic Analysis

Sample No.	Per cent									
	Si	Mn	Fe	Mg	Cr	Al	V	Ca	Cu	Ag
1896	0.3	0.08	PC	0.2	0.04	0.07	0.003	0.1	0.09	0.008
1898	0.6	0.09	PC	0.6	0.08	0.05	0.006	0.4	0.09	0.0002
1992	0.1	0.07	PC	0.2	0.08	0.05	0.003	0.06	0.05	Tr
1993	0.2	0.07	PC	0.09	0.05	0.008	Tr	0.06	0.04	0.0007
1994	0.1	0.07	PC	0.08	0.05	0.01	Tr	0.05	0.06	Tr
	Ti	Ni	Co	Na	Zn	Sn	Mo	Nb	Cd	Pb
1896	0.003	0.3	0.08	Tr	Tr	ND	ND	0.3	--	--
1898	0.01	0.7	0.1	0.3	0.3	Tr	Tr	--	Tr	Tr
1992	0.002	1	0.1	Tr	Tr	Tr	ND	0.06	--	--
1993	Tr	1	0.1	Tr	Tr	Tr	Tr	0.05	--	--
1994	Tr	1	0.1	Tr	Tr	Tr	Tr	0.04	--	--

The principal metallic constituent is shown to be iron. The chemical determination of this element was made by analysing another set of metallics isolated from four samples.

There was considerable spread of values for the per cent metallics and for the per cent metallic iron, as shown in Table 4.

TABLE 4

Variation of the Total Metallics and Metallic Iron

Sample No.	% Total Metallics	% Metallic Iron
1896	8.37 [*] ± 0.62(11) ^{**}	7.77 [†] ± 0.54 (9)
1992	19.54 [†] ± 0.68(5)	19.15 [†] ± 0.23 (2)
1993	24.99 [†] ± 0.73(11) ^{**}	23.46 [†] ± 0.75 (3)
1994	23.01 [†] ± 1.22(5)	20.88 [†] ± 1.02 (3)

* This value is expressed as the average with the average deviation.

** The bracketed figure indicates the number of determinations. The high number of determinations resulted in part from data used in Table 1.

The second most abundant metallic element shown in the spectrographic report (Table 3) was nickel. The relationship of per cent metallics, metallic iron and metallic nickel, based on five iodine-methanol separations of No. 1995, is shown in Table 5.

TABLE 5

Relationship Among Total Metallics, Metallic Iron and Metallic Nickel

Isolation	% Total Metallics	% Fe ^o	% Ni ^o	$\frac{\text{Fe}^o}{\text{Ni}^o}$	$\frac{\text{Fe}^o + \text{Ni}^o}{\text{Total Metallics}} \times 100$
1	21.67	20.10	1.11	18.11	97.88
2	21.52	19.95	0.93	21.45	97.03
3	21.35	19.68	0.99	19.88	96.81
4	20.32	19.16	0.87	22.02	98.57
5	21.32	19.95	1.06	18.82	98.55

Since the ratio of iron to nickel is not constant and the ratio of the sum of iron and nickel to total metallics varies, these two metals must not be uniformly distributed throughout this sample.

However, the sum of iron and nickel constitutes at least 97% of the total metallics of this sample.

In order to obtain a clearer picture of the balance of the metallics, a partial chemical analysis of the following samples was undertaken, the results of which are given in Table 6.

TABLE 6

Other Metallics Found by Chemical Analysis

Sample No.	Per cent						
	Ni	Si	Al	Ca	Cr	Cu	Mg
1896	0.045 ⁺ - 0.020(6)	0.08	0.04	0.02	0.03	0.04	<0.02
1992	0.63	0.03	0.08	0.02	0.04	--	<0.01
1993	0.96	0.03	ND	0.03	0.04	--	<0.01
1994	0.86	0.02	ND	0.02	0.03	--	<0.02
1995	1.01 ⁺ - 0.08(6)	0.01	0.04	0.11	0.03	--	<0.02

It is obvious from Tables 3 and 6 that the balance of the total metallics is made up of many elements in varying small amounts.

The results obtained on the seventeen fused chromite ore samples are shown in Table 7. The average values, with the average deviation, are shown for total metallics, iron, nickel and chromium. The other related analyses as shown in Table 6 are not included.

TABLE 7

Analyses of Fused Chromite Ore Samples

Sample No.	% Total Metallics	% Fe ^o	% Ni ^o	% Cr ^o
315	2.20 ⁺ 0.01(3)*	1.91 ⁺ 0.01(2)	--	0.06(1)
1193	2.77 ⁺ 0.08(5)	2.43 ⁺ 0.01(2)	--	<0.04(2)
1895	2.46 ⁺ 0.06(3)	1.95 ⁺ 0.07(2)	--	0.02
1896	8.37 ⁺ 0.62(11)	7.77 ⁺ 0.54(9)	0.045 ⁺ 0.020(6)	0.03
1897	2.54 ⁺ 0.22(3)	1.83 ⁺ 0.02(2)	--	0.02
1898	3.41 ⁺ 0.38(8)	2.91 ⁺ 0.03(4)	0.036	0.02
1899	2.11 ⁺ 0.12(3)	1.69 ⁺ 0.14(2)	--	0.02
1992	19.54 ⁺ 0.68(5)	19.15 ⁺ 0.23(2)	0.63	0.04
1993	24.99 ⁺ 0.73(11)	23.46 ⁺ 0.75(3)	0.96	0.04
1994	23.01 ⁺ 1.22(5)	20.88 ⁺ 1.02(3)	0.86	0.03
1995	21.20 ⁺ 0.47(10)	19.38 ⁺ 0.53(8)	1.01 ⁺ 0.08(6)	0.03
1996	2.00 ⁺ 0.26(4)	1.61 ⁺ 0.27(2)	--	0.02
1997	2.03 ⁺ 0.17(3)	1.67 ⁺ 0.05(2)	--	0.01
1998	4.16 ⁺ 0.68(3)	3.95 ⁺ 0.65(2)	--	0.01
1999	3.01 ⁺ 0.21(3)	2.59 ⁺ 0.15(2)	--	<0.01
3027	1.12 ⁺ 0.12(8)	0.76 ⁺ 0.09(7)	--	0.01
3028	2.87 ⁺ 0.37(3)	2.27 ⁺ 0.12(2)	--	0.02

*The bracketed figure indicates the number of determinations.

3. Solubility of Carbides and Graphite in Iodine-Methanol Reagent

In a letter* from Canadian Refractories Limited dated June 4, Mr. L. Hodnett enquired as to the solubility of carbon in the determination of metallics.

Previous experiments have indicated that carbides of some elements are decomposed by the iodine-methanol reagent producing free carbon, with the metal cation going into the filtrate to be counted as a metallic.

Total carbon and graphite contents have been determined for several chromite samples.

TABLE 8

Total Carbon and Graphite Contents of Fused Chromite Ore

Sample No.	% Total Carbon	% Graphite
1895	0.053	0.033
1896	0.098	0.059
1897	0.085	0.079
1993	0.071	--
1998	0.058	--

These figures indicate 10 to 40% of the total carbon is combined; probably in the form of iron and/or nickel carbides. Since these compounds are usually decomposed in the iodine-methanol reagent, the metallic iron and nickel values shown in Table 7 are liable to be slightly greater than the true metallics quantities.

4. Conclusions

The iodine-methanol procedure provides a useful method of separating the metallics from the non-metallics in fused chromite ore. A minimum refluxing time of two hours must be employed; however, a longer refluxing is not detrimental and may be used if it is more convenient.

* See Appendix.

The metallic phase is composed principally of iron with minor amounts of nickel, and the balance consists of several other elements, which are present in small quantities.

Considerable variation was observed in the quantities of the various metallics as well as the sum of the metallics. This situation is probably caused by segregation of the metallic phase in the chromite matrix.

ACKNOWLEDGEMENTS

The author thanks the following personnel: Miss E. Kranck, for semi-quantitative spectrographic analysis; J.F. Rowland and E.J. Murray, for X-ray diffraction analysis; R. Donahoe and D. Steeves, who assisted with the iodine-methanol separations and subsequent analysis of the metallic phase.

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(Appendix follows on)
(pages 13 to 18.)

APPENDIX

Mineral Sciences Division,
A.T. Prince, Chief.

555 Booth Street,
Ottawa, 4, Ontario.
March 13, 1962.

Mr. H. Booth,
Canadian Refractories Ltd.,
Box 160,
Grenville, Que.

Dear Mr. Booth:

At the request of Dr. A.T. Prince, we are pleased to enclose a copy of an outline of the method used in our laboratory for the determination of metallics in fused chrome ore.

The seventeen hour period used for refluxing the sample just happens to be convenient and is not implied to be specific. Our practice has been to start the sample in the late afternoon and filter off the solution next morning. It could be that a much shorter period of refluxing may be adequate; but, as yet, we have not investigated this. No doubt, the degree of fineness of the sample will be an influencing factor.

At a later date, on the completion of more analyses and further investigations, we will be issuing a more comprehensive report, in which limitations, etc. of the method will be indicated.

Yours very truly,

(sgd.) W.L. Chase

OUTLINE OF HALOGEN-METHANOL METHOD FOR THE DETERMINATION OF METALLICS IN FUSED CHROME ORE

A one gram sample is refluxed in an all glass apparatus with ten grams of iodine and seventy-five millilitres of anhydrous methanol for seventeen hours (samples are started in the afternoon, allowed to reflux all night and filtered in the morning). After cooling, the solution is filtered on a dried, tared asbestos Gooch. The residue is washed with anhydrous methanol, dried at 110°C, cooled and weighed. (The percentage of the sample that is soluble is readily calculated).

The soluble portion (filtrate) contains the metallics and possibly a little free lime or magnesia which are slightly soluble in methanol.

The analysis of the metallic phase is carried out by evaporating the iodine-methanol from the above filtrate. The non-volatile residue is fumed into solution with perchloric acid. This resulting acid medium can be used directly for specific determinations or it can be made up to a definite volume and aliquotted for various analyses.

Determination of Metallic Iron:

The iron in the acid medium is precipitated with ammonium hydroxide, filtered and washed. The precipitate is then dissolved with hydrochloric acid, reduced with stannous chloride and titrated with N/10 potassium dichromate.

Determination of Metallic Chromium:

The chromium in the acid medium is titrated directly in a diluted solution with N/40 ferrous ammonium sulphate using an automatic titrator.

Mines Branch,
March 12, 1962
L.G. Ripley

CANADIAN REFRACTORIES LIMITED
Canada Cement Building, Phillips Square
Montreal 2, Que.

June 4th, 1962

Mr. L.G. Ripley,
Mineral Sciences Division,
Mines Branch,
Dept. of Mines and Technical Surveys,
555 Booth Street,
Ottawa, Ontario.

RE: HALOGEN-METHANOL METHOD FOR
DETERMINING METALLICS

Dear Sir:

Following my discussions with you in connection with the variations in the analyses of metallics in the fused chrome ore samples supplied to you by Guy Sirianni, I have discussed this matter with our chief chemist, Mr. J.A. Bradley, and he intends to do work on our head sample of your laboratory No. 1898. When we get any results we would be very glad to pass them back to you in comparison with results that you are getting.

One other thing has crossed my mind in connection with possible material present and this is magnesium. On checking the chemical analysis of the fused ore against the original feed, we find that the magnesia as well as iron oxide of the chrome ore has been reduced during the fusion. If the magnesia was not volatilized then possibly some reduction has occurred and this could be with the iron providing that magnesium and iron do form an alloy.

In dissolving out the metallics, would any carbon in the metallics dissolve? If so, would this be material that is missing in the analysis?

Yours very truly,

CANADIAN REFRACTORIES LIMITED

(sgd.) L. Hodnett,
Asst. Technical Director.

CANADIAN REFRACTORIES LIMITED
Canada Cement Building, Phillips Square
Montreal 2, Que.

June 12th, 1962

Mr. L.G. Ripley,
Mineral Sciences Division,
Mines Branch,
Dept. of Mines and Technical Surveys,
555 Booth Street,
Ottawa, Ontario.

RE: DETERMINATION OF METALLICS

Dear Sir:

Our Laboratory has run one analysis on the fused chrome ore and this is on the head sample corresponding to your laboratory number 1898. His results are as follows:-

% Metallics	3.26
Fe	2.98
Cr	0.02
Si	0.07
Ca	0.07
Al	0.11
Mg	0.06

If you have any results on your check on materials present, we would appreciate receiving them.

Yours very truly,

CANADIAN REFRACTORIES LIMITED

(sgd.) L. Hodnett,
Asst. Technical Director.

Mineral Sciences Division,
A.T. Prince, Chief.

555 Booth Street,
Ottawa, 4, Ontario.
July 12, 1962.

Mr. L. Hodnett,
Canadian Refractories Limited,
P.O. Box 1750, Station "B",
Canada Cement Bldg.,
Phillips Square,
Montreal 2, Quebec.

Re: Halogen-Methanol Method for Determining Metallics

Dear Sir:

Thank you for your letters of June 4 and June 12, 1962.

We have the following analysis of the metallic phase for laboratory number 1898.

% Metallic	3.41	⁺ 0.25 (8)
Fe	2.91	⁺ 0.03 (4)
Cr	0.02	(1)
Ni	0.036	(1)

Also, we have a semi-quantitative spectrographic analysis:

<u>Si</u>	<u>Mn</u>	<u>Fe</u>	<u>Mg</u>	<u>Cr</u>	<u>Al</u>	<u>V</u>	<u>Ca</u>	<u>Cu</u>	<u>Ag</u>	<u>Ti</u>
0.6	0.09	PC	0.06	0.08	0.05	0.006	0.4	0.09	0.0002	0.01
<u>Ni</u>	<u>Co</u>	<u>Na</u>	<u>Zn</u>	<u>Sn</u>	<u>Mo</u>	<u>Cd</u>	<u>Pb</u>			
0.7	0.1	0.3	0.3	Tr	Tr	Tr	Tr			

As to your query concerning the possibility that carbon was the unaccounted metallic, recent experiments have shown that the total carbon in these chromite samples is present at a level of less than 0.1%.

.../2

Therefore, from the above values it appears that the difference between total metallics and metallic iron is composed of many elements which are present in small quantities.

A detailed report on the Determination of Metallics in Fused Chromite Ore is being prepared and should be available soon.

Yours very truly,

(sgd.) Leonard G. Ripley

LGR:DV