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The decomposition and analysis of chrome spinel. A survey of some published techniques

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SUMMARY. Examination of published procedures for the decomposition and subsequent analysis of chromite and chrome ores shows some to be unnecessarily complicated and time consuming. Others fail to yield consistent and reproducible results. Decomposition is rapidly and effectively accomplished using the peroxide frit technique of Rafter. Chromium may then be removed and determined volumetrically allowing the rest of the analysis to proceed along conventional silicate lines. Fe^{2+} is determined by oxidimetry following digestion with a mixture of phosphoric and sulphuric acids in the presence of ceric sulphate.

THE refractory nature of the chrome-rich spinels $(Fe,Mg)(Cr,Al)_2O_4$, together with their high concentrations of Fe^{2+} and Cr^{3+} have long presented serious problems in obtaining reliable analytical results for this group. A variety of methods of decomposition and subsequent analytical procedures have been proposed. Apart from Hartford's (1953) appraisal of analysis of industrial chrome ores no attempts have been made to evaluate these different methods, although some of the resulting analyses suggest deficiencies.

Irvine (1965) shows that some published analyses of chromite depart widely from the ideal formula. Although some spinel minerals are known to possess cation deficient structures, non-stoichiometry is generally slight and could certainly not account for the majority of excesses in both R^{2+} and R^{3+} reported. Irvine assumed that the iron ratio $Fe^{3+}:Fe^{2+}$ was probably the major single source of error. Although this is probably true there is some evidence that points to error in Cr^{3+} and Al^{3+}, which may be directly related to the methods of analysis.

The purpose here is to review some of the wet chemical procedures suggested for chrome-spinel that have been examined in this laboratory for reliability, effectiveness, and general applicability. It is hoped that the following observations may be of assistance to analysts confronted with analysing occasional small batches of chromite samples. Recourse to instrumentation and rapid colorimetric procedures (Dinnin, 1959) may be had where large numbers of samples are to be determined.

Preparation of samples

Mineral separates of chrome spinel may be purified and concentrated by a combination of magnetic separation, use of heavy liquids, and chemical destruction of silicate gangue with hydrofluoric, hydrofluorsilicic, and hydrochloric acids. In some rocks a range of spinel compositions exist and care must be taken that the final concentrate is not merely the most resistant, dense, or magnetic fraction.

In grinding ore samples containing a high proportion of silicate gangue silicates tend to concentrate in the finer fractions (especially < 350 mesh) and the use of of a splitter is necessary to achieve a representative sample. If the sample is too coarse the time for complete decomposition may be prolonged. Yet grinding must not be excessive or decreases in Fe^{2+} and Cr^{3+} occur (Hartford, 1953) and the sample absorbs moisture that is not removed by drying at 100 °C (Hillebrand and Lundell, 1929). All samples used in the present study were ground to pass B.S.S. 150 mesh with fifty per cent passing B.S.S. 240 mesh. Mineral separates were ground by hand in an agate mortar as was the final grinding of ore samples. This avoided the very fine comminution achieved in a mechanical vibratory grinder.

Decomposition of sample

The problem of opening chrome-spinel ores and mineral samples is common to all methods of analysis employing solutions. Few reagents effect complete decomposition in a single attack, many require long fusion or solution times, and some introduce serious contamination either from the container or by way of undesirable ions that complicate subsequent analytical procedures. It is most desirable before selecting a particular reagent that the chemist know both the approximate composition of the spinel from physical determinations (e.g. Richmond, in Stevens, 1944) and the nature of any gangue that may be present. For example, chrome hercynites dissolve readily in a greater variety of fluxes than do picrochromites and chromites, while pyroxene gangues are markedly less susceptible to attack by some fluxes than serpentinized olivine gangues.

The ideal flux or solvent is usually one that completely and efficiently decomposes the sample in a single attack, produces a solution in which the nature of the anions may be determined and introduces no troublesome contaminants. Such fluxes exist but unfortunately are not generally applicable.

Published procedures may be divided into those employing acid solvents and those employing acid or alkaline fluxes. The general advantages and disadvantages of these techniques are fully explored in standard treatises such as Kodama (1963) and Maxwell (1968).

Acid solvents. Most common mineral acids have little effect on chromite at ordinary pressures, but phosphoric acid slowly decomposes chrome spinels although introduced phosphate ions may complicate subsequent analytical procedures.

The 72·6 % azeotrope of perchloric acid (B.Pt 203 °C; $D = 1{\cdot}71$) has long been known to attack chromites and is used in several procedures. Complete dissolution is achieved at boiling point in 6 to 8 hours. However, care must be exercised to avoid low and erratic values of Cr_2O_3 and SiO_2. Commercial acid shows some variability in strength and quality and must be brought to constant boiling at 203 °C before adding the sample. Also some commercial acids show high chromium blanks—up to

0·4 mg/l. Chromyl chloride is readily volatilized from the boiling solution and considerable care is necessary to prevent its loss; oxidation of chromium to a single valence state is seldom complete (Schumacher, 1960); attack on silicate gangue is usually incomplete.

Alkaline fluxes. A wide variety of fluxes for chromite have been proposed but few reasons are given for preferring any one over another. The common basic fluxes of routine silicate work (carbonates, hydroxides, tetraborates) are generally unsatisfactory, even in the presence of oxidizing agents. Sodium carbonate/borax mixture is effective with aluminous spinels but chrome-rich varieties require fine grinding and long and repeated fusions. Malhotra (1954) reported that sodium carbonate could achieve complete decomposition of chromites in two hours if oxygen was passed through the fusion mixture.

Molten peroxide provides the most efficient flux for all spinels and has a very short fusion time (5 mins). Details of the method are given in Dinnin (1959). Unfortunately, few containers resist attack: Platinum, nickel, iron, silica, and porcelain containers all add large amounts of undesirable contaminants to the sample; zirconium ware adds up to 5 mgm Zr/g Na_2O_2 (Petretic, 1951) although this amount decreases with repeated use of the container; silver crucibles are only slightly attacked by molten peroxide at dull red heat and experiment shows these to be preferable to zirconium ware. Care must be exercised in the use of silver as the M.Pt of silver is only 960 °C. It may be added (although not recommended) that quite coarse grains of chromite (~40 mesh) are completely attacked in five minutes.

Rafter (1950) showed that a high temperature was unnecessary for attack, decomposition being achieved by fritting an intimate mixture of peroxide and spinel at 480 °C for 7 minutes. Platinum containers suffer no attack at this temperature. 200 mesh samples are generally used. Pyroxenes in the gangue may resist attack and have to be separately dealt with.

Petretic (1951) tried a peroxide/sugar-carbon explosion technique as a means of reducing attack on crucibles but the method seldom achieves complete decomposition of spinel in a single fusion and requires a double amount of peroxide.

Acid fluxes. Van der Walt (1938) employed potassium pyrosulphate for chromite and Ross, Foster, and Myers (1954) used the sodium equivalent. The relative merits and demerits of these two fluxes have been discussed frequently and the method of Ross *et al.* is generally unsuitable. The potassium salt slightly attacks platinum at full heat and gold crucibles should be used. The silicate gangue is often incompletely decomposed, especially if pyroxenes are present, and a second carbonate fusion is often necessary. An alternative technique here is to destroy the silicate fraction with hydrofluoric acid, add sulphuric, bring to fumes and finally fuse the residue with pyrosulphate.

Khundkar and Quadir (1953) employed a modified Kjeldahl digestion that proves more efficient than a direct pyrosulphate fusion. Digestion may be performed in heavy pyrex or silica beakers over low flame since excessive heat is not required. Silica determinations appear unaffected. Gangues are readily attacked although pyroxenes occasionally pose a problem.

Mixed fluxes. A variety of mixed fluxes have been recommended for attack on spinel ores, e.g. $NaHSO_4/NaF$; Na_2CO_3/soda-lime; Na_2CO_3/MgO; Na_2CO_3/CaO. These proved singularly ineffective in dealing with ferro- and magnesio-chromites.

Main portion of analysis

Treatment of the solution resulting from decomposition of sample and digestion of the fusion cake may follow a variety of paths, which to some extent are predetermined by the flux and digestive medium employed. Four procedures are representative of the variety available.

The technique of van der Walt (1938) uses a pyrosulphate fusion followed by digestion with hydrochloric acid. Silica is determined in the usual way and aliquots of the resulting filtrate are used for determination of other elements. Results are generally good and the method may be considerably enhanced by using modern procedures such as complexiometric titrations for CaO and MgO and a silver or Jones reductor for iron.

Ross, Foster, and Myers (1954) employed a stepwise semiclassical procedure after $NaHSO_4$ fusion and digestion with H_2SO_4. This method gives erratic results. Silica tends to be low and R_2O_3 (and hence alumina) high. Examination of the data of Ross *et al.* by Irvine (1965), for example, showed that of nine analyses two contain a pronounced excess of R^{3+} and one an excess of R^{2+} over the model spinel formula. Error may also result from the use of a sulphuric acid solution which is known to be troublesome in mineral analysis (Maxwell, 1968).

Malhotra and Prasada Rao (1956) used an alkaline fusion to open the spinel. Leaching the cake with water allows separation of all chromate together with some silicate and aluminate from the other constituents and reduces the rest of the procedure to that of a routine rock analysis. This method yields good results and has been combined with Rafter's peroxide frit technique in this laboratory. In all but two of nine analyses made by Malhotra and Prasada Rao the RO/R_2O_3 ratio in the structural formulae lies between 0·95 and 1·05 (the limits of experimental error); the other two ratios are 1·07 and 1·09. Six analyses of New Caledonian chromites made by the author using this technique had RO/R_2O_3 ratios between 0·98 and 1·03.

A perchloric acid digestion was used by Bilgrami and Ingamells (1960). The solution is diluted and filtered to remove silica. The R_2O_3 group is then separated with aqueous ammonia, ignited, and weighed. Subsequent procedures are complicated by the behaviour of manganese and chromium at this stage. This procedure failed to yield good values for silica when applied to a standard chromite in the present study. Values were consistently low and showed little agreement: 2·68, 3·82, 2·75 (preferred value 4·25). An explosion occurred in a fourth attempt and is believed to result from failure in the method to remove perchloric acid from the filter. Bilgrami and Ingamells made their final wash with 2 % $HClO_4$. If 1:1 HCl is used this hazard may be overcome.

The R_2O_3 precipitate obtained by their method invariably contains not only Fe_2O_3, Al_2O_3, TiO_2, and V_2O_5 but some silica as well as some chromium and manganese, which must be separated and determined following a pyrosulphate fusion of the oxides. For these two reasons, and the fact that adequate precautions are not taken to prevent loss of chromyl chloride during the lengthy digestion, the method has not been pursued further. Several of Bilgrami and Ingamells's analyses show marked deviations from the ideal formula, e.g. their analysis 2 has a ratio $RO/R_2O_3 = 1{\cdot}36$. It is not accepted that these variations arise from oxidation of the spinels during crystallization, as they claim.

Notes on individual constituents

Silica. The silicate fraction of chrome ores varies between wide limits. Unless special precautions are taken conventional gravimetric procedures return low values of SiO_2. This is particularly evident in the majority of published procedures, which use only a single dehydration. Low values of SiO_2 result in high values of RO in calculation of the structural formula and RO/R_2O_3 ratio. Dinnin (1961) has shown that a significant proportion of silica remains in solution, particularly in 'purified' chromite samples containing 0·3–1·0 % of SiO_2. Colorimetric procedures developed by him invariably return higher values than do gravimetric. Dinnin also notes that the lowest values of total silica result where decomposition is made with perchloric acid due in some part to failure to totally decompose the silicates. Hydrochloric acid dehydrations give better results although some silica remains in solution, part of which may be recovered by fuming with sulphuric acid. In a 1 g sample of chromite containing 1·03 % SiO_2, 4 mgm remained after dehydration with hydrochloric acid of which 2 mgm was recovered by using sulphuric. (Dinnin, p. D398)

In our laboratory good results on the analysis of chrome ores were obtained by using the technique of Ritchie (1962). The bulk of the silica is dehydrated and filtered off and the portion remaining in solution determined colorimetrically using the reduced silicomolybdate.

Chromium. The oxidation–reduction titration of chromium is the most widely used technique. A critical examination of the procedures involved, given by Hartford (1953), includes corrections to procedure necessary for ores containing significant vanadium. The most reliable and simple technique is that of Bryant and Hardwick (1950); elimination of any of their steps leads to erroneous results.

Cr_2O_3 may be determined on a separate sample (e.g. Dinnin, 1959) or on an alkaline extract from either a peroxide fusion, a peroxide frit, or a Na_2CO_3/O_2 fusion.

Total iron is usually determined by oxidimetry of a reduced solution after removal of chromium. Reducing agents vary (e.g. stannous chloride, silver reductor), but have little effect on the final result. Methods mainly vary in the point at which iron is determined in the over-all analysis scheme. Hartford (1953) uses a separate sample; van der Walt (1938) employs an aliquot of the filtrate obtained after removal of silica; Malhotra and Prasada Rao (1956) and Ross *et al.* (1954) estimated iron in R_2O_3 following a pyrosulphate or peroxide fusion of the oxides. Results are fairly consistent.

Calcium and magnesium. Most published techniques employ gravimetric procedures using the filtrate obtained after elimination of silica, chromium, and R_2O_3. The use of E.D.T.A. titrations or E.G.T.A. supersedes these methods with a consummate saving in time (e.g. see Maxwell, 1968).

Alumina. Traditionally, as in silicate procedures, aluminium is determined by difference after determinations of other elements of the R_2O_3 group. Any errors in these determinations are reflected in the figure for Al_2O_3. Some of the recent advances in the direct determination of alumina in silicates appear applicable to spinel, e.g. Bennett, Hawley, and Eardley (1962); this eliminates the time-consuming R_2O_3 determination.

Manganese and titanium. Colorimetric procedures are recommended although titanium may be determined with E.D.T.A. in the presence of hydrogen peroxide using Xylenol Orange as indicator (pH 1–2). Unfortunately no ore with reliable TiO_2 values is available to confirm the method.

Ferrous iron. The problems associated with the determination of Fe^{2+} in refractory minerals have been extensively reviewed by numerous writers (e.g. Maxwell, 1968). Dinnin (1959) gives an excellent coverage of three methods applicable to chromite. Dinnin's method (A) based on that of Shein (1937) and employing the modification of Goswami (1957) was used in the current study.

Shein's technique involves digesting the sample in a mixture of concentrated sulphuric and phosphoric acids (2:1) containing a known excess of V_2O_5. The reduced vanadium after digestion is determined with standard $KMnO_4$. It is important that the acid/vanadium solvent be preoxidized before use but even so results obtained by the method tend to be high, as V_2O_5 is not perfectly stable in the hot acid.

Goswami (1957) employed ceric sulphate in place of vanadium pentoxide, using a 4:1 mixture of phosphoric and sulphuric acids at 300 °C. Consistent and reproducible results were obtained in the present laboratory not only on standard chromites but also on standard silicate rocks and Analar standards. Mixtures of samples and acid are put to heat overnight and titrated after cooling and dilution the following morning. The only disadvantage so far encountered with the method is considerable corrosion of the laboratory oven.

Summary of preferred procedures

Decomposition of sample: Peroxide frit (Rafter, 1950) or peroxide fusion in a silver crucible (Dinnin, 1959).

Cr_2O_3: Bryant and Hardwick (1950); also detailed by Dinnin (1959).
Al_2O_3: Bennett *et al.* (1962).
FeO (*total*): Silver reductor (Maxwell, 1968).
FeO: Shein (1937) as detailed by Dinnin (1959)—use ceric sulphate in place of vanadium pentoxide.

CaO *and* MgO: E.D.T.A. titration (Maxwell, 1968).
MnO *and* TiO_2: Colorimetric methods (Maxwell, 1968, or Ritchie, 1962).
SiO_2: Ritchie (1962).

Results of analyses made by these methods of British Chemical Standard Grecian Chrome Ore (No. 308) are shown in table I. It is interesting to note that the values determined for silica and magnesia using the above techniques are slightly higher than the preferred values, which were mainly obtained by gravimetric procedures. The figures for alumina are slightly lower where this element was determined directly.

TABLE I. *Analyses of B.C.S. Grecian chrome ore (No. 308) by methods outlined in text with preferred values in col. 4*

	1	2	3	4
Cr_2O_3	41·60	41·42	41·48	41·5
FeO*	15·32	15·33	15·38	15·3
SiO_2	4·32	4·33	4·25‡	4·25
Al_2O_3	19·34	19·32	19·50§	19·4
CaO	0·33	0·31	0·36	0·34
MgO	16·52	16·58	16·49	16·4
TiO_2	0·12	0·12	0·13	0·14†
MnO	0·12	0·14	0·12	0·15†

* Total iron as FeO.
† Preliminary figures.
‡ Double dehydration for SiO_2.
§ Determined by difference.

Conclusions

Experimental work in the present study appears to lead to the following conclusions: Widespread use of perchloric acid digestions in quantitative analytical procedures needs careful reassessment. Recently some independent geochemical studies were drawn to the author's attention. Chromium and to a lesser extent nickel and vanadium determinations of soils and plant ash showed much higher values where hydrofluoric/nitric digestions had been employed than where perchloric digestions were used. Table I in Kodama (1963, p. 7) gives a good guide to the relative volatilities of the different elements in perchloric and perchloric/halogen acid mixtures.

There is a most unfortunate lack of suitable international analytical standards in the field of non-silicate mineralogy. No spinel ores with satisfactory analyses of minor constituents were available, and only two samples could be found with reliable ferrous/ferric ratios.

It is regrettable that some methods that proved deficient in the current study have been uncritically accepted in the literature; a notable example is the republication of Bilgrami and Ingamells's perchloric acid digestion procedure by Maxwell (1968).

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