

CHEMICAL PHASE ANALYSIS

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In many scientific investigations and technical operations it is necessary to know not only the total amount of an element of interest but also the amount of its different valencies, combinations or mineralogical forms. The different phases or forms of an element can usually be observed of course by microscopical examination, X-ray diffraction or other physical means. The frequent difficulty of obtaining by these techniques a rapid quantitative measure of the phases present has led to the development of many chemical procedures, based principally on a selective solvent, a chelate, resin or other isolating agent. The chemical approach, though it may suffer from certain deficiencies in accuracy and precision, has the merit of quickly providing a reasonable satisfactory result. It does not require expensive and complicated instruments or workers with long experience in the interpretation of data. The popularity of chemical phase analysis in industrial practice, therefore, is not difficult to understand.

The accuracy and precision of chemical phase analysis are influenced by the following variables :

- 1) Composition of the sample
- 2) Particle size of the sample
- 3) Concentration of solvent
- 4) Temperature of solution
- 5) Agitation of suspension
- 6) Atmosphere of reaction
- 7) Time of contact of reagents

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Composition of the sample : In phase analysis, a selective solution step is usually employed to isolate one major phase from the mixture. For instance, in 5% sulphuric acid saturated with sulphur dioxide, the oxidized forms of copper such as malachite, azurite, tenorite, and chrysocolla dissolve whereas sulphide copper is insoluble. The presence of cuprit or native copper, however, complicates such a differentiation because half the cuprite and all the native copper are reported with the sulphides.

The mineralogical composition or physical form of a sample also has an important bearing on phase analysis. If the element of interest occurs in a finely disseminated state in a hard, impervious siliceous gangue, its extraction by leaching solvents will be more lengthy and less efficient than if that element occurred in the form of larger particles interspersed among a soft, porous carbonate gangue.

Particle size of the sample : As with all chemical analyses, the representative sample must be finely pulverized to enable the reaction between solvents and solids to proceed to completion within a reasonable period of time. The nature of the material has an important bearing on the degree of comminution required. As a general rule, the sample should be -100 mesh; in finely disseminated in gangue, the sample should be -200 mesh or even finer.

Concentration of solvent : The quantity of reagent used to bring about a preferential dissolution of the desired constituent, provided of course that it is adequate for this task, is usually not a critical parameter in phase analyses. In methods where reducing conditions are maintained by a reagents like sulphur dioxide, or oxidizing conditions by hydrogen peroxide, care must be taken that the reagent are fresh enough to provide an excess for the entire reaction period.

Temperature of solution : Most of phase analyses show a range of solution temperatures from room to about 100°C.

Leaching time : The time of contact of the selective solvent with the sample may range from a few minutes to many hours. It will depend on several factors: particle size, temperature agitation, and solubility. The accessibility to the solvent of finely disseminated ore minerals in a gangue of sulphide particles coated with oxide, or of metallic grains surrounded by oxide, is also important in specifying a leaching period. In general, a sample of -100 or -200 mesh size, frequently stirred in a solvent at a temperature about 50°-60°C, will usually not require a leaching period longer than 15-30 minutes. If, however, the desired element occurs in a finely divided state in an impervious gangue, a much longer period may be necessary to attain virtually complete extraction.

Agitation of the suspension : Some form of agitation to improve solid-liquid contact is usually employed in phase analyses. It may vary from shaking the vessel manually for several seconds every 10-15 minutes during the leaching period, to continuous agitation on a shaking machine for the entire period of the leach.

A vigorous mechanical agitation promotes aeration and oxidation of the sample solution. If this is undesirable in phase analysis, agitation may be provided by bubbling a stream of nitrogen through the solution.

Atmosphere of Reaction : The differentiation of phases by selective solvents may be carried out in air, or in an inert atmosphere. If the reaction is not sensitive to oxidation the case of operation in air dictates its use. When an inert atmosphere is necessary, carbon-dioxide is frequently used. Alternatively an inert atmosphere may be maintained by a flow of nitrogen from a cylinder of the compressed gas.

This review is confined to the quantitative analysis of some elements of importance in phase analysis.

Calcium

Free CaO is extractable from $\text{Ca}_3(\text{PO}_4)_2$, CaF_2 , CaCO_3 , CaSO_4 , or calcium silicate ores with an aqueous sucrose solution^[1, 2]. Calcite can be selectively dissolved in the presence of fluorite by 5-10% acetic acid^[3,4]. Approximately 0.3% of the fluorite also dissolves and therefore the appropriate correction should be made to the calcite result.

Aluminium

The differentiation of aluminium oxide from metallic aluminium is important in drosses and powders of the aluminium industry.

The following methods may be used to determine metallic aluminium from alumina

1. Treatment of the sample with methanol-bromine mixture to dissolve aluminium metal, leaving the oxide intact^[5, 6, 7 8]
2. Reaction of the metallic copper produced by the aluminium metal and determination of the excess copper left in solution^[9,10]

Iron

Fe, FeO, Fe_2O_3 and Fe_3O_4 in reduced ores. Metallic iron can be selectively extracted from reduced iron ores with a solution of mercuric chloride in water^[11] or alcohol^[12] by copper sulfate solution^[13,14]. The use of bromine in alcohol is superior to that of mercuric chloride^[15].

To determine FeO and Fe₂O₃ in reduced iron ores a sample from which metallic iron has been removed is dissolved in hydrochloric acid in an inert atmosphere. The iron^[11] in solution is determined by titration with dichromate or vonadate ^[16]. The same solution is analysed for total Fe and Fe(111) is obtained by difference.

Magnetite is selectively extracted from mixtures with hematite by 1% hydrochloric acid and phosphoric acid and an oxidant such as hydrogen peroxide or permanganate^[17,18]. In products of reduction roasting containing metallic iron and ferrous oxide, magnetite has been selectively dissolved in a boiling alcoholic solution of stannous chloride ^[19].

Iron oxide in iron sulphide ores, Magnetite has been determined in the presence of chalcopyrites by heating and stirring for 5 min in 1:1 phosphoric acid^[20].

Iron sulphide ores, pyrrhotite can be determined in the presence of pyrite by dissolution in 4% stannous chloride in 6M hydrochloric acid ^[21].

A knowledge of the magnetite content of mattes and slags is important in copper metallurgy. One procedure depends on the rapid dissolution of sulphides in a hot nitrochlorate solution, and the relative insolubility of magnetite in the same condition^[22]. It is essentially a method for the determination of ferric iron, the magnetite content being calculated from the ferric iron value of the assumption that all the ferric iron present is in the form of magnetite.

Ferrous and ferric iron in rocks and ores. For the determination of ferrous iron, the sample is decomposed with sulphuric-hydrofluoric acid mixture with the exclusion of air and direct titration of ferrous iron ^[23]. Ferric iron in rocks and ores is in general assumed to be the difference between the total and ferrous iron.

Copper

Oxide copper or acid soluble copper : Oxidised copper mineral can be extracted from sulphide ores with a reagent consisting of 2g of sodium sulphite and 1g of phenyl acetic acid in 20 ml of acetone and 100 ml of 3% H_2SO_4 ^[24].

Chrysocolla : The determination of chrysocolla, a copper silicate in copper ores is of importance to a few procedures because it is not amenable to normal floatation processes. Treatment of copper ores with 1% unithiol solution dissolves azurite, malachite and cuprite ^[25]. Chrysocolla can be extracted from the residue with a 2% sodium sulphite solution in 3% sulphuric acid. Copper sulphides are unattacked.

A different approach to phase analysis of copper ores has been published ^[26]. Malachite is dissolved by boiling the sample for 2 hours in a nitrogen atmosphere with alkaline 10% sodium potassium tartrate. The residue is washed with 1% NaOH and boiled for another 2 h in an oxygen atmosphere to dissolve cuprite. Striving the residue for 3 h with 5% H_2SO_4 and 2% ferric sulphate dissolves 50% of the chalcocite. The third residue is then boiled for 10 min with 5 ml acetic acid and 100 ml of saturated silver sulphate, and stirred for 4 hours to dissolve the rest of the chalcocite and bornite. The final residue is chalcopyrite.

Differentiation of copper and its oxides in powders : Cuprous oxide is dissolved selectively in 3N ammonium chloride at 95°C under a carbon dioxide atmosphere. After filtration, the residue is digested with 6N sulphuric acid at 70°C to dissolve cupric oxide, metallic copper remains in the final residue ^[27].

Manganese

Metallic manganese : One hour extraction at 70°C with 30ml of methanol containing 5g mercuric chloride dissolves metallic manganese.

Several workers have proposed methods for manganese oxides of various valencies when these are present together. Heat the sample with 20 ml of 6N ammonium sulphate for 20-25 minutes with stirring, filter and wash. Manganese derived from MnO is in the filtrate. Treat the residue for 1 hr at 70-75°C with 15 ml of a solution containing 15 g metaphosphoric acid in 100 ml of sulphuric acid. Filter, wash with 25% sulphuric acid and determine manganese in the filtrate, this represents manganese derived from Mn₂O₃. Place a separate sample in a known volume of standard sodium oxalate solution add 10 ml of 25% sulphuric acid and keep at 70°C until dissolved. Filter, wash and titrate the excess sodium oxalate with 0.1N potassium permanganate to obtain MnO₂ ^[28].

The determination of Mn₂O₃ can also be carried out by heating the sample on a water bath for 1 hr in a mixture of 100 ml of 10% sodium pyrophosphate and 2 ml of 1:1 sulphuric acid, filtering, adding a known amount of ferrous ammonium sulphate and titrating the excess with standard potassium permanganate. Mn₃O₄ is obtained by difference ^[29].

Sulphur

Sulphide in the presence of sulphate is usually determined by evolution of hydrogen sulphide on treatment of the sample with acid ^[30]. Hydrogen sulphide gas is absorbed in ammoniacal cadmium chloride solution and finally determined iodometrically. Sulphate may then be determined directly as barium sulfate or as the difference between total and sulfide sulphur.

Pyrrhotite sulphur can be determined in the presence of pyrrite sulphur by its evolution as hydrogen sulphide by a 4% stannous chloride solution in hydrochloric acid (1+1) ^[21]. This reagent may, however, also partially decompose pyrite and it is recommended that a solution of hydrazine in 4N sulphuric acid be used instead ^[31].

Zinc

In the extractive metallurgy of zinc, oxidized ores require a treatment differing from that for sulphides, and it is important to differentiate these forms.

The most successful selective solvent for complex non-sulphide zinc ores is 2% by volume sulphuric acid saturated with sulphur dioxide. Oxidized zinc minerals such as smithsonite, Willemite, Zincite and hemimorphite are easily separated from sphalerite as sulphide ore is nearly insoluble ^[32].

Finely divided zinc called zinc powder or zinc dust, is a familiar article of commerce, zinc oxide likewise has many uses. In both those substances it is important to know the content of zinc oxide as well as total zinc. In general, the determination of zinc oxide in zinc powder or dust or in commercial zinc oxide, can be carried out by the solution of zinc oxide in solvents such as ammonium acetate, ammoniacal ammonium chloride. Zinc sulphide and metallic zinc are not attacked and remain in the residue.

Metallic zinc in zinc dust, zinc oxide etc. metallic zinc reduces ferric iron to the ferrous state, whereas zinc oxide does not. The ferrous solution can be titrated with a standard solution of potassium permanganate or dichromate to give a measure of the metallic zinc present.

Silicon

Free silica : The dust of pulverized rock is treated successively with hydrochloric, hydrofluosilicic acid and hydrofluoric acid. Carbonates are decomposed by hydrochloric acid and silicates by hydrofluosilicic acid; free silica is virtually unattacked and remains in the residue to be dissolved by hydrofluoric acid and determined by loss of weight on volatilization.

Free silica in coal dust has been found by the following procedure: carefully ignite the sample in a muffle until all carboaceous matter is destroyed. Treat the ash with hydrochloric acid until action ceases, dilute, boil filter and wash. Boil the residue with 25% sodium sulphide, cool dilute, filter and wash. This residue contains silica, metal sulphides and sesquioxides; remove the latter two with a mixture of 6N hydrochloric acid and 6N nitric acids, filter, wash and weight the residue of free silica. Obtain a true value of the latter by the loss in weight through the classical evaporation with hydrofluoric acid sulphuric acid ^[33].

An important procedure for free silica is based on the fact that pyrophosphoric acid dissolves all silicates but not quartz. This is currently the most popular phase analysis for free silica ^[34].

A rapid method for free silica in clay, kaolin and bauxite consists of fusion with potassium bisulphate or pyrosulphate for 3-4 minutes at 800°C, digestion in hydrochloric acid 1:2 and filtration. The free silica remains in the residue ^[35].

The determination of the forms of silicon in water has been reported ^[36]. Traces of silicon in the water for high pressure, steam generating equipment of modern power station may be important "Reactive Silicon" includes those forms of silicon, mainly monomeric

and dimeric silic acid that react with ammonium molybdate in 10 minutes under the conditions of the method. Molybdisilicic acid is reduced by 1-amino 2-naphthol 4 sulphonic acid containing sodium sulphite and potassium metabisulphite.

Lead

A number of methods for phase analyses of lead minerals and ores have been proposed. The sample is treated with 25% sodium chloride solution to dissolve all the lead sulphate and then with 15% ammonium acetate solution in 3% acetic acid to dissolve PbCO_3 . Successive treatment of the residue with 2% sodium hydroxide solution and ammonium acetate solution extracts the combined lead of PbCrO_4 and wulfenite, PbMoO_4 . Pyromorphite $-\text{Pb}_5(\text{PO}_4)_3 \text{Cl}_2$ and vanadinite $\text{pb}_5 (\text{VO}_4)_3 \text{Cl}$ are then extracted with a 25% solution of sodium chloride in 0.5% hydrochloric acid. The galena Pbs in the residue may be dissolved with a 25% solution of sodium chloride in 6% ferric chloride solution ^[37].

Lead dusts have been subjected to phase analyses. Lead oxide is removed in acetic acid, lead sulphate in sodium chloride solution, metallic lead in copper nitrate solution and lead sulphide by a mixed solution of sodium chloride and ferric chloride ^[38].

It has been found, when PbSO_4 and PbCO_3 are determined in the presence of galene and pyrite that pyrite increases the solubility of galena. The effect can be suppressed by adding ascorbic acid and cupric chloride.

Conclusion

The accuracy and precision of phase analyses are usually not as high as those of conventional elemental chemical analyses. The accuracy usually varies inversely with the complexity of the material. A differentiation between metallic and oxide zinc in material containing only these phases would yield results closer to the true values than would a determination of metallic cobalt in a material containing metallic oxide, and sulphide cobalt together with many compounds of other metals.

Despite its limitations, chemical phase analysis has provided valuable information in many fields for a long period, particularly in the mining and metallurgical industries. For process control, an approximate result obtained quickly can be very useful; a highly accurate result which becomes available only after considerable time is usually of little value.

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