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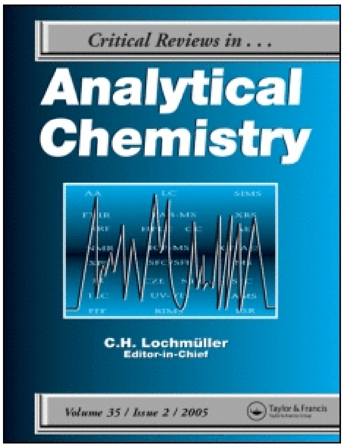

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DECOMPOSITION PROCEDURES IN INORGANIC ANALYSIS

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I. INTRODUCTION

Decomposition of solids involves a series of reactions, which transform the original substance and produce quantitatively new phases. The decomposition usually results in the formation of solutions or melts; sometimes new solid phases are formed. The reactions are generally accompanied by the formation of gaseous phases. The conversion of the original component is either complete (usually in fusion decompositions) or an undecomposed fraction with the original or a changed phase composition remains (in acid decompositions).

During fusion, new solid phases with structure similar to glasses are formed, the composition of which is quite different from that of the original substance. As the cooling period of the melts is very short, the melts turn into glasses and the "true" crystalline phase is not commonly found in the solidified melts. These new formed glasses are readily soluble in water or in aqueous solutions of acids.

Another type of decomposition reaction involves substances in a heterogeneous solid-gas system. During the reaction, changes occur in the solid phase (mostly oxidation or reduction); the products formed are also more readily decomposable with acids than is the original substance. Sometimes, a gaseous or volatile compound is a product of the reaction and can be easily separated from the system.

In the present study, various procedures for the decomposition of inorganic materials are critically evaluated. Generally, natural mineral materials have been selected for this purpose because of their considerable variability and behavior different from that of their synthetic equivalents. Compounds prepared in the laboratory are usually available in a better defined form in both chemical composition and structural state. On the other hand, mineral substances represent much more complex materials because of isomorphous element displacement, the presence of inclusion segregated phases, and growth irregularities. The problems of decomposition can better be demonstrated on such complicated systems, especially the selection of the technique with consideration of the intended analytical procedure.

One reason this field of analytical chemistry has been selected as the main topic of study is our long years of experience in this area. Without an experimental background, it is difficult to evaluate various decomposition techniques to assess their efficiency, and to propose an optimum decomposition procedure for various materials being analyzed.

II. DECOMPOSITIONS UNDER PRESSURE IN CLOSED SYSTEMS

Transfer of substances into solution is a basic operation which, together with the analytical method used, determines the precision and accuracy of the results obtained. Decompositions of natural and industrial inorganic materials represent such an important stage in the analysis that special monographs have recently been devoted to this subject.[1,2] At present, a new decomposition technique in a closed system at an elevated temperature and pressure is becoming increasingly important in analytical practice. The pressure decomposition of substances is based on heating the sample and the solvent in a closed vessel, in which the pressure increases due to increasing temperature. At higher temperatures and pressures the activity of mineral acids increases, resistant solid phases are dissolved, and the whole dissolution process is accelerated. Operations under increased pressure, common in the synthesis of inorganic and organic substances, were first applied to geological materials by Jannasch[3-5] at the end of the 19th century. He decomposed a rock sample in a platinum vessel inserted in a sealed glass tube. This method of dissolution of inorganic substances did not give good results, due to poor efficiency and considerable corrosion of the platinum vessel and the glass used. Modern techniques of pressure decompositions chiefly involve heating of sealed hard glass ampules and sample dissolution in a vessel tightly closed in a metallic autoclave. The reaction vessels themselves are mostly made of polytetrafluoroethylene (Teflon® PTFE), or platinum and its alloys, or gold. With only slightly increased pressure and temperature, the decomposition can be carried out in tightly closed polypropylene, polycarbonate, or Teflon vessels without the outer metallic mantle.

A. Substance Dissolution in Sealed Glass Tubes

The pressure decomposition involves heating of substances with solvents sealed in hard-glass tubes placed in open or closed steel cylinders, using a compensating pressure. This pressure is attained by placing certain substances in the steel cylinder which are turned into gases on heating and give rise to approximately the same pressure as that formed by the reaction mixture inside the glass tube. Compared with substance dissolution in autoclaves (with Teflon inserts), this system has a number of advantages:

1. Relatively easy attainment and maintenance of a high working temperature (usually up to 300°C) under a pressure above 100 atm.
2. Decomposition procedure is simple and does not require complex apparatus.
3. The possibility of handling large series of samples.
4. Practically unlimited stability of solutions in the hermetically sealed system in an inert atmosphere and maintenance of the individual ions in a defined valence state (e.g., Fe^{2+}).
5. Minimal extent of redox reactions between the ampule walls and the ions in the solution.

The main disadvantage of this pressure decomposition technique is partial leaching of the alkali metal ions, silicic and boric acids, and possibly other components dependent on the glass composition. Therefore, this technique of substance dissolution is unsuitable for determination of certain components. Dilute HF solutions and alkali hydroxides also cannot be used for dissolution in glass tubes. For series work, the analyzed samples are sealed in hard glass, the surface of which must not be damaged; otherwise, an explosion may occur during heating. Heated tubes without a metallic mantle are used for pressures up to ca. 2 MPa. Because these pressures are easily obtained even at relatively low temperatures (especially when gaseous reaction products are formed), the tubes are placed in metallic cylinders with a tight screw closing for safety. A volatile liquid (e.g., an organic solvent or water) or solid carbon dioxide which exhibits a practically linear pressure increase over the whole experimental temperature range is added to the cylinder.[6] Manipulations with glass ampules and methods for their filling as well as application possibilities have been reviewed and are discussed in basic monographs.[6-8]

Since the original but not very successful experiments of Jannasch,[3-5] only the study of Wichers et al.[9] has brought attention to the practical applicability of pressure decompositions. The prolonged effect of HCl on a number of resistant natural and synthetic oxides and silicates was systematically studied (250°C for 16 to 48 hr). Under these reaction conditions, cassiterite, spinel, and chromite, as well as some silicates (e.g., cordierite, sillimanite, amfibol, muscovite, etc.), were completely dissolved. Among plagioclases, the basic members of the series are more easily decomposed, while albite and oligoclase remain virtually undissolved. Rocks were generally only partially decomposed. These experiments were supplemented by Brazilian authors[10] who studied the solubility of certain industrially important raw materials. Even oxides previously ignited at a high temperature (e.g., Al_2O_3, BeO, SnO_2, and HfO_2) are dissolved following prolonged treatment with HCl at 230 to 250°C.[7,11] Analogously, single crystals of corundum and hematite, which need not even be finely pulverized,[7] can be dissolved. Even prolonged action of HCl or H_2SO_4 did not lead to dissolution of $BaTiO_3$. Rutil single crystals[12] resist the 24-hr action of concentrated HCl; only about one half of a 50-mg sample is dissolved.

Decomposition of complicated oxidic substances under pressure has often been used in the study of ferrites. Generally, lower temperatures were employed and the decompositions were carried out in sealed tubes without an external pressure. The procedure proposed by van Oosterhaut and Wisser[13] was utilized by Goerter[14] to determine the reducing effects of ferrites. Basically, the studies are related to the procedure originally developed in 1860 by Mitscherlich,[15] who decomposed silicates in a sealed tube with diluted H_2SO_4, in order to determine Fe(II). The accuracy of the results obtained was verified by reference analyses[16] after the decomposition of the substances with HF. The procedure was modified by Hillebrand[17] and Hillebrand and Stokes.[18,19] Kleinert successfully applied the Mitscherlich method to analyses of Ni ferrites.[20] This kind of cubic ferrites is very difficult to decompose using HCl under atmospheric conditions; thus, the substance must be dissolved in a sealed ampule.[21,22] The solution obtained is used for the determination of active oxygen; the material need not be finely pulverized, so there is no danger of contamination. This kind of decomposition is applicable to various ferrite types; phosphoric acid[23] was successfully used as the solvent for the determination of Fe. Substances with similar structures, e.g., chrommagnesites, are readily dissolved[24] by heating with diluted H_2SO_4 (1 + 3). Complicated oxides and some other uranium components contained in uranium ores are readily dissolved after being heated for 2 hr with HCl at 200°C; the procedure was tested for rapid extraction of uranium from sandstones.[25]

Pressure decompositions were successfully used in the preparation of solutions of certain metals of the platinum group, especially Rh and Ir and their alloys containing Pt, which cannot be dissolved even by prolonged action of aqua regia at atmospheric pressure. Dissolution of these metals by chlorination in open systems or by fusion is much more difficult and often leads to contamination of the prepared solutions. The principal works in this field[9,26] were published from 1940 to 1944. Chlorine, bromine, fuming nitric acid, and hydrochloric acid (possibly in combination with chlorate) were used for oxidative dissolution. Since the gaseous reaction products substantially increase the pressure in the tubes, protective metallic mantles with a compensation pressure are employed. During filling with oxidizing solutions or liquid Cl_2 and during opening, the ampules are strongly cooled with ice.

A special technique[27,28] for rich ores and chemical dressing products has been developed at the National Institute for Metallurgy in Johannesburg. The ores and the matte are decomposed by aqua regia after preconcentration of the Pt metals by reductive fusion to a Pb button. Simple decomposition of the button with high silver content by aqua regia in a beaker is very difficult; buttons obtained by fusion of chromites are also difficult to dissolve. The Pb button is decomposed in a mixture of HCl and fuming HNO_3 for 3 hr at 200°C. A reducing fire-assay technique is also employed for treatment of residues of solutions with high contents of Cu, Ni, and Fe and low concentrations of the Pt metals. Rich platinum ores are directly attacked by a mixture of HCl, fuming HNO_3, and bromine, as are the residues after the extraction of mattes. The simultaneous presence of bromine and fuming HNO_3 facilitates the complete oxidation of sulfides without formation of elemental sulfur, whose presence makes complete sample dissolution in aqua regia more difficult. Decomposition by HCl and Cl_2 is chiefly used for the preparation of defined standard solutions; atomic absorption spectometry (AAS) is almost exclusively employed as the analytical method for the final determination. Decomposition in a sealed tube with HCl and $NaCl_3$ was recently employed for the determination of Ir and Ru in rhodium sponge.[29] The complete decomposition takes 6 hr at 250°C. The dissolution of finely ground buttons was described by Zachariasen,[30] and the decompositions of the Pt metals in sealed ampules has been generally evaluated in Beamish's excellent monograph.[31]

Pressure decompositions were successfully applied to resistant high melting components, e.g., boron carbides.[32,33] Aluminium nitride[34] is decomposed within 6 to 24 hr by diluted sulfuric or hydrochloric acid in an ampule at 230°C.

A special decomposition technique is used for barytes, because heating of the mineral with concentrated HI at 300°C for 48 hr leads to complete sulfate reduction to soluble sulfide.[35] However, alkaline feldspars and acidic plagioclases are attacked to a lesser degree than they are by HCl under identical conditions. On the other hand, anorthite and sillimanite are completely decomposed. Selenium dioxide, which melts at 300°C under a pressure of 9×10^5 Pa, was tested as an effective fusion agent.[36] Niobium and tantalum(V) oxides are dissolved in the melt at this temperature. Al_2O_3 and Cr_2O_3 form pyroselenates, which can be dissolved in an alkaline solution or in HCl. SiO_2 does not react even after 16 hr of heating to 420°C; SnO_2 forms pyroselenate which is insoluble in the melt.

Some components can be released from the analyzed substance by pressure decomposition with H_2O. Fluoride present in a corundum single-crystal plate (1 cm^2, thickness 0.5 mm) is quantitatively released by heating with 5 ml H_2O at 240°C for 24 hr. This reaction is caused by ion exchange of fluoride for hydroxyl; the crystal surface is preserved for other physical tests.[37] A similar exchange reaction was also observed with barium titanate.[38]

B. Decompositions in Autoclaves

New models of pressure vessels with a plastic reaction vessel closed in an autoclave metallic mantle have been proposed, since the solutions obtained by substance dissolution in glass ampules cannot be used for the determination of the main components (especially in silicate analysis). This new technique, still in development, found wide use in analytical practice as late as the second half of the present century. Its subsequent rapid development was the result of:

1. Mastering of the production technology of organic polymers[39] which are exceptionally resistant to mineral acids even at high temperatures and pressures (i.e., polytetrafluoroethylene, fluorinated ethylenpropylene (Teflon FEP), polypropylene, etc.).
2. Rapid development and the requirements of new instrumental analytical techniques (e.g., AAS, mass spectrometry, etc.) in which high contents of salts in the solution make the measurement difficult.
3. Increased demands for the determination of submicrogram amounts of elements; fusion decompositions cannot be employed because of high concentrations of impurities in the fusion agent and undesirable reactions of the melt with the crucible walls.
4. Efforts to work out a universal process for complete dissolution of mixtures of minerals, which would make it unnecessary to consider the phase composition of the analyzed substances; the solution obtained could be used for the determination of both major and minor elements.
5. New procedures for the preparation of ultrapure acids for decompositions.
6. The difficult technology of the production of very pure fusion agents and resistant materials for fusion crucibles.

The pressure decomposition technique was used widely only after introduction of polytetrafluoroethylene (PTFE, Teflon) as a material for the reaction vessel. This method of dissolution was employed as early as 1958 by Riley[40] for the determination of the alkali metals in rocks containing resistant minerals. After common dissolution in a mixture of hydrofluoric and perchloric acids, the isolated undecomposed fraction containing tourmaline, staurolite, rutil, corundum, etc. was decomposed by HF in an autoclave for 3 to 4 hr at a temperature of 150°C.

Ito[41,42] proposed a construction consisting of a steel autoclave with a PTFE crucible insert; and he decomposed many minerals using a mixture of HF and H_2SO_4. The decomposition is remarkably efficient: tourmaline, axinite, and cornerupine are dissolved within 2 to 3 hr at 240°C. A reaction time of 4 to 8 hr is sufficient for complete destruction of the crystal lattices of ilmenite, chromite, magnetite, columbite, and tantalite. Dissolution of rutil and baddeleyite takes a long time (12 to 16 hr). The sample decomposition is complete after 10 hr if only HF is present. Heating to 250°C in a mixture of HF and $HClO_4$ leads[43] to complete dissolution of beryl, cyanite, staurolite, pyrite, chalcopyrite, and pyrrhotite within 1 hr; only 35% of topaz is decomposed. The behavior of many minerals and inorganic materials (mullite, andalusite, beryl, lepidolith, zircon, corundum, quartz, cassiterite, chromite, spinel, ZrO_2, and $BaTiO_3$) during dissolution in a closed system at 240°C, using mixtures of HF, HCl, H_2SO_4, $HClO_4$ and H_3PO_4, has been reviewed in the above study.[44] The reaction rate is strongly affected by continuous stirring of the mixture. The decomposition is especially suitable for complete analysis of glass-making sand. The sample need not be pulverized; a grain size below 1 mm is sufficient, so the danger of contamination during grinding is avoided. Simultaneously with the decomposition of quartz, resistant materials which usually carry impurities in glass-making sands (e.g., chromite and tourmaline) are completely dissolved.

An autoclave with an aluminium mantle was used by Wahler.[45] He studied the decomposition process rate with HF and $HClO_4$ at 200°C under stationary decomposition conditions. Corundum, rutil, spinel, zircon, tourmaline, topaz, and some garnets are dissolved slowly or incompletely even if the reaction time is prolonged and the grain size decreased.[46,47] According to Wahler,[45] the Finnish Geological Survey[48] uses decomposition of spinel, beryl, and tourmaline in an Al autoclave with a mixture of HF and $HClO_4$ to determine Be by AAS. The decomposition of 5- to 15-mg rock samples for the determination of trace elements[49] by flameless AAS was successfully carried out in the same type of pressure vessel. Dissolution of resistant rock-forming minerals, such as tourmaline (schorl), sapphirine, or staurolite, was studied by Popov[50] in a pressure vessel of his own construction.

One of the most difficult problems of pressure decompositions is complete dissolution of zircon; Doležal et al.[44] did not succeed in decomposing this mineral under the conditions specified by Ito.[41] As the data concerning the trace concentrations and isotopic composition of Th, U, and Pb in zircons are employed for geochronological purposes, the decomposition of this resistant mineral must be effected using acids without introducing impurities from fusion agents into the reaction mixture. According to the method developed in the Carnegie Institute, 50 mg of zircon are dissolved after 1 week[51] when heated at 220°C in 2 to 3 ml of 48% HF. Quite clear solutions are obtained. The decomposition is employed routinely in many important geochronological laboratories of Geological Surveys (e.g., in Finland or the German Federal Republic). Using very pure hydrofluoric acid, the blank amounted to 0.5 to 5×10^{-9} g Pb^{2+}, while it increased to 0.2×10^{-6} g Pb^{2+} with fusion with sodium tetraborate. The $UO_2{}^{2+}$, Th^{4+}, and Pb^{2+} ions are separated on ion exchangers after the dissolution, and their concentration is determined by mass spectrometry using the isotope dilution method. After a short dissolution period in an autoclave (3 hr) even at temperatures of 280°C, zircon was detected microscopically in the undecomposed residue. This mineral is not completely dissolved even in fuming 71 to 75% HF after 20 hr at 280°C; Borchert and Donderer[52] had to employ a temperature of 400°C in a gold-plated autoclave.

For the determination of the isotopic composition of U, Th, and Pb in geological materials and chondrites, Arden and Gale[53,54] recommend a HF pressure decomposition, possibly with the addition of HNO_3. The dissolution takes from several hours to up to 2 days at a temperature of 110 to 200°C. Even pieces of meteorites (~1 g) are decomposed. The reaction mixture is evaporated in a stream of purified air or nitrogen. After dissolution of the residue in 6 *M* HCl, the pressure decomposition is usually repeated at 120 to 180°C. In order to suppress contamination, the Teflon vessel is first leached with 6 *N* HCl at a temperature of 120 to 180°C. Provided that zircon does not contain an economically significant amount of uranium, a temperature of 130 to 170°C is sufficient for complete dissolution of the uranium ore in HF and aqua regia; the time required is 50 to 100 min, depending on the analyzed material grain size.[55] Recently, various decomposition methods for uranium ores with variable uranium contents bound in resistant minerals have been statistically evaluated.[56] The efficiency of pressure decomposition (with HCl + H_2O_2 and H_2SO_4 + $KMnO_4$) was compared with the generally used procedure for the destruction of mineral materials by solutions of HF, H_2SO_4, and HNO_3 at atmospheric pressure. These results show that decomposition with HF and the two experimentally checked pressure decomposition procedures have an almost equivalent effect.

Bernas[57] managed to suppress interferences in the subsequent AAS determination of main rock components by judicious combination of reagents and the decomposition technique. A 0.05- to 0.30-g sample was dampened with 0.5 ml of aqua regia and dissolved in 3 ml of 48% HF at a temperature of 110°C for 30 to 40 min in a pressure vessel of his own construction. The solution was transferred into a plastic beaker using a Teflon mouth, and the fluoride precipitate formed was dissolved by adding 2.8 g H_3BO_3. The solution was diluted to 100 ml and stored for 2 hr in a glass volumetric flask. After this time, gradual hydrolysis of HBF_4 occurred with liberation of HF, causing corrosion of the glass. The universal character of the decomposition and a favorable effect of HBF_4 in the final AAS determination were verified by other authors. The technique[57,58] was employed for decompositions and analyses of tectites, lunar soils,[59] clays,[60] marls, raw powder and other cement raw materials[61] and ceramic materials,[62] oxides,[63] various minerals, ores, and slags;[64-67] for the determination of cationic components and phosphates in natural phosphates[68-70] (especially when the phosphorus is bound to organic matter);[71] for decompositions of isolated magnetic and nonmagnetic meteorite fractions;[72] and for the determination of nitrogen in metals and nitrides.[73,74] A material decomposition by a mixture of HF, $HClO_4$, and HCl in a special pressure vessel was used for the determination of microgram amounts of this element in very pure Ta, Nb, Zr, and Cu. Ammonia formed in the reaction is determined by coulometric titration.[75]

F. J. Langmyhr and co-workers have recently dealt systematically with the combination of pressure decomposition methods with AAS. In a specially constructed reaction vessel, they studied the dissolution of ores, rocks, minerals, and inorganic products.[76,77] The vessel type was selected according to the decomposition temperature used. At temperatures below the boiling point of azeotropic hydrofluoric acid (112°C for 38.26% HF) a polypropylene or polycarbonate Erlenmeyer flask should be used; this method (1) permits an increase of the temperature up to 130°C and dissolution of the many siliceus materials within 5 to 30 min. Resistant material must be decomposed in a Teflon vessel tightly closed in an Al-block and heated to temperatures in the range of 150 to 250°C, with continuous stirring with a Teflon-coated magnetic stirring bar. The decomposition was effected with 38% HF alone or in a mixture with HCl, $HClO_4$, or HNO_3 (Method 2). The excess HF is bound by adding H_3BO_3 or an aluminium salt. The main components and SiO_2 are determined simultaneously. The procedure developed was employed for the quality control of glass-making sands[78] (Method 1) and the major and minor components of bauxites[79] (Method 2). The newly proposed procedures have found use in the analysis of ferrosilicon[80] (Method 2), alkaline feldspars[81] (Method 1), iron ores and slags[82] (Method 2), and sulfidic minerals[83] (Method 2) and rocks.[84] No loss in SiO_2 occurs when using the two decomposition techniques. Decompositions of various mineral phases have been reviewed in Langmyhr's work.[85]

A number of authors have dealt with the AAS determination of major, minor, and trace elements in soils and rocks after an autoclave decomposition.[86-93] Grobenski[94] employed a Perkin-Elmer pressure vessel for this purpose and determined traces of Co, Cr, Cu, Ni, Pb, and V in addition to the major components in international geochemical reference materials. With ultrabasic rock peridotite PCC-1 and dunite DTS-1, the sample weight had to be decreased to 0.05 to 0.1 g and the reaction time and the temperature increased to 30 min and 150°C, respectively. Granite, andesite, and granodiorite are decomposed more easily; a 0.2-g sample is completely decomposed within 10 to 30 min at 110 to 150°C. The precipitate formed is dissolved in a H_3BO_3 or an aluminium salt solution. If a volatile component is to be determined, the reaction mixture is diluted with a saturated H_3BO_3 solution immediately after opening of the reaction vessel. When destruction of the crystal lattice of clay minerals (halloyisite, caolinite) and talc occurs as a result of mineral acids attack (HCl, H_2SO_4, H_3PO_4) at 240°C in a Thermobox® autoclave, a gel-like silicic acid with a minimum content of impurities[95] is precipitated in the absence of HF. Decomposition in the Parr-bomb was proposed for the subsequent isolation of Rb and Sr from lunar rocks[96] from the area of the Sea of Tranquility. A 0.15-g rock sample spiked with ^{87}Rb isotope is dissolved in HF, HCl, and $HClO_4$ in an autoclave with a Teflon insert at 120 to 140°C. In order to decrease the possibility of contamination, the analyzed material was only very roughly pulverized in a boron carbide mortar.

Pressure decomposition was successfully applied to analyses of other inorganic materials, such as glass,[97] slag,[98] iron ore[99] and steel,[100] chiefly for the microanalysis of isolated inclusions and the determination of zirconium[101] and aluminium.[102] A similar procedure is also effective in analyses of ores and concentrates of the platinum metals and in the preparation of the corresponding standard solutions. It is recommended for decompositions of ores and products containing iridium and osmium:[103] The material is heated in a mixture of HF and HCl (1 + 10) at 250°C for 3 hr, and the insoluble residue is further decomposed by fusion. Some platinum metals, which are difficult to dissolve under normal conditions, are easily transferred into solution using HCl and HNO_3 in an autoclave. When heated at 180°C, as much as 0.5 g Rh and 0.25 g Ir are dissolved, as well as a Pt-Rh-Ir ternary alloy. The procedure is also successful in solution preparation in the analysis of reforming catalysts.[104-106]

Pressure decompositions are rarely used for differentiation among the individual valence forms of polyvalent elements (most frequently for the determination of FeO) in rock-forming minerals. The reaction mixture containing HF is heated in a tightly closed Teflon vessel in a boiling water bath or in a metallic autoclave with a Teflon insert. The procedure developed by Riley and Williams[107] for the determination of FeO in milligram amounts of isolated minerals has been successfully used for the determination of FeO in amphibole, biotite, chamosite, and some rocks. Complete decomposition is attained in a closed Teflon tube after 40 min dissolution in a mixture of HF and H_2SO_4 in a boiling water bath. Kiss[108] employed a Teflon vessel of his own construction for the same purpose. The decomposition of amphibole, magnesite, eclogite, basalt, and diabase is complete after 60 min in a boiling water bath. A minor technical alteration can modify the reaction vessel for pressure decompositions at 200°C. The same author determined the FeO concentration in resistant minerals and rocks after dissolution in a pressure microvessel[109] at a temperature of 100 to 200°C.

The direct determination of FeO in solutions after pressure decomposition (at a temperature higher than 130°C) is not reliable. To obtain reliable results, the mineral is usually decomposed by HF or H_2SO_4 in the presence of an oxidant, whose excess is back-titrated with an Fe^{2+} salt. These reagents are unstable at high temperatures and pressures and often react with the vessel walls or with some rock components. The HF-H_2SO_4-$KMnO_4$ system originally proposed by Ito[41] has not been successful in analytical practice. Successful methods of determining FeO in resistant minerals (chromite and staurolite) were obtained by dissolving the mineral in HF and H_2SO_4 in the presence of excess ammonium vanadate:[110] 0.25 g of the mineral is weighed into a Teflon crucible and 1 to 2 ml H_2O, 10 ml 0.1 *M* ammonium vanadate in H_2SO_4 (1 + 1), and 5 ml 40% HF are added. The crucible is placed in the autoclave and is heated for 6 hr at 200°C. The reaction solution is transferred into a vessel containing 2 to 3 g H_3BO_3, and excess vanadate is back-titrated with an Fe^{2+} salt. The vanadate stability is checked by simultaneous blank determination. Although the results obtained by this method are not comparable with values obtained by other chemical methods (they agree well with Mössbauer spectroscopy), they yield the maximum FeO contents for schorl, which are apparently most probable.

Experience with decompositions of other minerals has shown that vanadic acid also acts as a decomposing agent, and its oxidizing properties cause valence changes at the mineral-liquid interface, thus accelerating the crystal lattice destruction. For example, the decomposition of ferrilmenite (iserine) by a mixture of HF and H_2SO_4 was incomplete in the absence and complete in the presence of vanadic acid under otherwise identical conditions; chromite behaves similarly. The strong effect of this mixture suggested the possibility of using this decomposition procedure for unpulverized materials. The solubility of isometric grains of certain garnets (almandine), amphiboles (kersutite and actinolite), and pyroxene was studied. It was found that decomposition is complete under the given conditions and the residue does not contain an undecomposed original phase. However, the results of the determination fluctuated depending on the degree of homogeneity of the mineral. While garnets (four different samples) exhibited relatively identical results, a greater variation was observed with zonal amphiboles (four types). In any case, this procedure is advantageous for the determination of FeO, as the gross errors connected with the preparation and homogenization of analytical samples are eliminated. The experimental results showed that pulverization of certain garnets (i.e., almandine) leads to almost complete FeO oxidation.

Experiments with glass ampules with pieces of Teflon immersed in solutions of ferric and stannic salts[111] have indicated that the Teflon vessel itself exhibits considerable reducing effects. Therefore, the solution obtained by the decomposition of cassiterite in hydrochloric acid contained predominantly stannous ions.[44]

Reactions often occur during dissolution of inorganic substances, leading to the formation of volatile compounds of the analyzed components (Ge, As, B, Si, etc.). The results can then be scattered even under rigidly controlled reaction conditions. Sometimes these volatile elements are built into the crystal lattices of resistant minerals. Therefore, the reaction mixture temperature cannot be substantially increased in common decomposition procedures for these substances, because the ion or molecule formed immediately reacts with the decomposing agents, giving rise to volatile compounds. Part of the element being analyzed is then lost or part of the sample remains undecomposed; the results obtained are subject to a negative systematic error. Dissolution in a closed system under pressure eliminates these disadvantages. This procedure is chiefly employed in the determination[58,77,79-83,112] of silicon in minerals, rocks, and sulfidic ores; the SiO_2 content (present as soluble H_2SiF_6 after decomposition with HF) is then determined by AAS or spectrophotometry. A satisfactory closed vessel can also be made of polyethylene[113] and the decomposition can be carried out at 65°C.

Material dissolution in an autoclave has also been used as a control procedure for detecting the extent to which the component to be determined is lost during fusion or acid decomposition in an open system. Pressure decomposition generally yields the highest results which are very close to the true value. The above procedure has been used for the evaluation of methods for the determination of trace amounts of Re in molybdenite ores and concentrates[114] (Re_2O_7 volatilizes at 227°C). The results obtained by AAS after decomposition with HNO_3 with added $NaClO_3$ were compared in an open and a closed system and after alkaline-oxidative fusion. The dissolution of rocks in the determination of Te was studied analogously.[115] When the concentration of the component to be determined is low, it is preconcentrated by sorption on an ion exchanger (together with Se, Bi, Sb, and As). The ion exchanger is decomposed prior to the final determination by fuming nitric acid in a pressure vessel[116] (150°C for 4 hr). Losses in Ge as the volatile chloride or fluoride are prevented if the sulfidic material is dissolved in a Teflon crucible closed in a pressure vessel.[117] The use of an autoclave prevents losses in As in the analysis of anorthite, petalite, muscovite, beryl, and some rocks. These materials are decomposed by an HF + H_2SO_4 ($HClO_4$) mixture for 1 hr at 150°C, and sulfides are preoxidized by $HClO_4$. To determine As in TiO_2 using destructive activation analysis, the analyzed oxide is dissolved in HF (125°C for 3 to 4 hr) in a Parr pressure vessel complemented by a special aluminium heating block. The tightness of the pressure vessel was tested using the ^{76}As isotope, in view of the formation of volatile AsF_3. More than 88% of the As present passes into the solution and a small part remains deposited on the Teflon vessel.[119]

There is no danger of volatilization of Hg in the dissolution of geological samples in a closed pressure vessel; the method was successful in the determination of nanogram amounts[120] in diabase, andesite, pyrite, and other sulfides. The decomposition of Hg is complete following 5 to 10 min treatment with HF in mixture with HCl and HNO_3 at 120°C. The fluoride precipitate is dissolved in a saturated H_3BO_3 solution, and the Hg content is determined by flameless AAS. Although mercuric salts volatilize easily, the autoclave is closed very tightly and there are no losses, even with submicrogram amounts of mercury. Copper ores, concentrates, and tailings[121] are decomposed by H_2SO_4 and $KMnO_4$ (possibly with HF) at 150°C for 1 hr. The process of quartz and glass[122] dissolution in 40% HF solutions (in the presence of $HClO_4$) was controlled by ^{7}Be, ^{75}Se, ^{131}I, and ^{203}Hg isotopes. The losses observed were mostly below 1%; they amounted to as much as 4% only with iodine. Iodine diffuses into the Teflon vessel walls and can be removed again by boiling with HNO_3. Nitrogen gases also diffuse into Teflon during prolonged use. In the "cold vapor" technique (for the AAS determination of Hg), decomposition in a pressure vessel (Parr) with HF and aqua regia yielded higher results[123] than parallel dissolution in a H_2SO_4+HNO_3 or HNO_3+HCl mixture in the presence of $KMnO_4$. On the basis of the results of analyses of sediments with high

SiO_2 contents (clays and soils), hornfels, and andesite, it can be assumed that part of the mercury is associated with silicates and can be released only by destruction of the crystal lattice. Mercury and its compounds deposited on membrane filters in the control of atmospheric pollution are also released by oxidation with HNO_3 in a pressure vessel.[124] Closed polypropylene bottles suffice for prevention of Sn volatilization in decompositions of deep sea sediments, manganese concretions, and red clays[125] by HF and HCl. The organic matter is oxidized by H_2O_2, which facilitates liberation of Sn from sediments. One gram of the rock sample is dissolved in 20 ml of 11 *M* HCl and 5 ml HF by heating in a boiling water bath.

The use of pressure decomposition for the AAS determination of trace elements in coal is noteworthy.[126] Organic substances (50 mg) are oxidized by fuming HNO_3 at 150°C for 2.5 hr; the destruction of the inorganic fraction is completed by adding HF after 15 min (at the same temperature). The Cd content[127] in coal and the SiO_2 content in animal charcoal were determined under analogous conditions.[128] Procedures developed by Kaiser et al.,[129] Paus,[130] Holak et al.,[131] and Krinitz and Holak[132] were successful in determining volatile components in biological materials.

In analyzing ultrapure substances, the dissolution process is the principal source of contamination and consequent error. These substances can be dissolved without contamination in special pressure vessels using Teflon. Decomposition in a closed system considerably decreases contamination, and enables separation of the volatile reaction product directly from the reaction vessel in an inert gas stream.[133,134]

Hydroiodic acid was also employed for autoclave decompositions. Its reducing effect (210°C for 3 hr) causes conversion of baryte to soluble barium sulfide. Natural lead(II) sulfate (anglesite) is decomposed analogously. Thus, alkaline fusion can be avoided; both minerals are decomposed only negligibly by mineral acids under normal pressure.[135]

Reagents other than strong inorganic acids were employed only occasionally in pressure decompositions: 30% potassium hydroxide readily dissolves corundum at 240°C. In the solution obtained, the silicate is present as the monomer, which can be advantageously utilized in the spectrophotometric determination of SiO_2 as a silicomolybdenum complex. Pure quartzes can be dissolved analogously, and defined standard SiO_2 solutions can readily be prepared. The quartz grains need not be crushed; the dissolution is complete and sufficiently rapid with 1- to 2-mm grains. Complete decomposition of halloyisite was achieved using 30% NaOH under identical conditions.[95]

Prolonged (1 week) extraction of pieces of alkaline granite and granodiorite with dilute solutions of NaOH and NaCl and with tap or distilled water at 150°C was utilized by Ronge and Bernhardsson[136] in determining the resistivity of rock walls of underground containers of industrial hot waters. The authors determined the major rock components in the extracts by AAS; tap water was most corrosive.

In Teflon-covered autoclaves, pressure decompositions can be carried out at temperatures up to 250°C (the work[52] gives 280°C; Nalge manufacturer's literature[39] quotes 205°C), which sometimes prevents complete sample decomposition even if the reaction time is considerably prolonged. Further increasing of the temperature causes substantial deterioration of the physical properties; above 300°C, the formation of toxic gaseous decomposition products may occur. Therefore, autoclaves covered with gold[52] or platinum were constructed.[137,138] The first attempts date from the end of the last century; however, the Jannasch device[3-5] was not successful because of serious technical shortcomings. In 1965 May and co-workers[137,138] proposed a construction for a pressure vessel (made of the nichrom alloy) covered with a Pt foil or an alloy of 80% Pt and 20% Ir, which is more resistant than Pt alone. The temperature in the 3.5-ml reaction space can be increased up to 425°C. After 18 to 20 hr, 1 to 1.5 ml of 40% HF (possibly with the addition of H_2SO_4) dissolves 25 mg of zircon or 100 mg of phenakite, staurolite, and beryl. The crystal lattices of garnet, chrysoberyl, cyanite, and sapphirine are completely destroyed; G-1 and W-1 standard rocks are also readily dissolved. Chromite, corundum, and hematite are dissolved in HCl in approximately the same time.

The decomposition of zircon is not complete even at 280°C, according to Borchert and Donderer;[52] therefore, they proposed the use of a gold-covered autoclave. During the action of fuming 71 to 75% HF, the reaction temperature must not decrease below 400°C for 30 min, in order to decompose 99% of the mineral. In an 85-ml autoclave it is possible to decompose as much as 10 g of zircon; the gold layer is more resistant to corrosion caused by fuming HF than is platinum.

The development and wide application of certain instrumental methods (especially AAS) have been manifested in an increased effort to construct and experimentally test new autoclave types. Although they were originally only prototypes, some pressure vessel types have been so successful in practice that they are manufactured commercially. The reactions inside the autoclave proceed either under stationary conditions or are hastened by rotation of the vessel, by rocking, or by stirring with a magnetic stirring bar encased in Teflon; the vessel is then heated directly on the magnetic stirrer plate. A new modified autoclave type was proposed by Langmyhr and Paus.[139] The metallic mantle is made of a resistant Al alloy; the temperature can be increased up to 200°C and regulated to ±0.5°C. Wahler[45,46] employed pure Al for the autoclave construction. Mineral materials can be decomposed at a temperature of 200°C and a pressure of 2 MPa in the Teflon crucible insert. An apparatus for simultaneous decomposition of 20 samples was described by Tereshchenko.[117] The dissolution (180°C) is hastened by rocking of the pressure vessel. The effectiveness of this decomposition technique was verified for the determination of Li, Cs, and Pb in rocks. An interesting dissolution procedure has been described by Knoop.[40] Ten Teflon test tubes each containing a 50 mg- sample and 0.5 ml 40% HF were inserted into the pressure vessel. Doležal et al.[44] proposed a thermostatted unit in which six samples are simultaneously decomposed and the dissolution process is accelerated by rotating the pressure vessel; the device is commercially available from Geotest under the name Thermobox®.[141] The construction of pressure vessels based on this principle was variously modified.[39,142] A cooling system[143] can also be built into the aluminum autoclave mantle, thus accelerating the manipulation after decomposition. The device is commercially available from Perkin-Elmer. The same company[144] manufactures Autoclaves 2 and 3. The decomposition is carried out on a metallic plate by stirring. The maximum operation temperature is 160°C and the pressure is 5 MPa; the device has a safety valve. Although pressure decomposition with $HClO_4$ is often used for rocks, the prospectus points out the danger of explosion.

One of the principal manufacturers of pressure vessels is the Uniseal Company,[145] whose constructions are based on Bernas' works.[57,58,146-148] The working temperature is 110 to 180°C, and the maximum permissible pressure 8 MPa; the volume of the internal vessel is as much as 75 ml. Teflon-covered autoclaves are also supplied by the Parr Company;[149] the device was used for the decomposition of lunar rocks[96] and coal.[126] The pressure can also be measured during dissolution by an inbuilt manometer; this device from the Spex Company[150] can be used at temperatures of up to 180°C. The Juniper Company[151] recommends their autoclave for dissolution of cassiterite, columbite, asbestos, cyanite, and other materials. The Berghof Research Institute manufactures autoclaves[152] (according to Tölg)[34] with electronically controlled decomposition temperatures. Steel pressure vessels lined with Teflon are heated in an aluminium block to 250°C for long periods and to 300°C for short periods; however, the Teflon vessels become distorted at temperatures higher than 280°C. A device for simultaneous decomposition of ten samples is supplied commercially; more detailed information can be found in the appropriate journals.[153,154]

Rantala and Loring[155] proposed a Teflon pressure vessel without an outer mantle because the autoclave price is relatively high. The decomposition of a 1 g sample (standard reference rocks of the U.S. Geological Survey and sea sediments) is complete within 1 hr at a boiling water bath temperature. Organic materials remain undecomposed,[156] the residue being less than 3%. The device is available commercially from the Morrison Company.[157] Decompositions under mildly increased pressure in a Teflon crucible with a screw lid are employed in the laboratories of the French Geological Survey.[158]

The decomposition technique under slightly increased pressure has been used in analytical laboratories because of its simplicity and the availability of the instruments. Its introduction has been made possible by progress in organic polymer technology. Polycarbonate and polypropylene in particular have found successful use among new plastics; screw lids ensure sufficient tightness of the vessels,[39,158] so that volatile compounds in the analyzed components are not lost during heating. This decomposition technique (in polyethylene vessels) was successfully employed to determine SiO_2 content in fluorite raw materials. Most common dissolution procedures lead to losses of SiF_4 formed by the reaction of CaF_2 with the silicates and quartz present.[159] Transparent polypropylene bottles were recommended for the decomposition of silicate rocks.[160] The finely powdered rock (0.1 g; -300 mesh) is dissolved in aqua regia and HF on a boiling water bath. Dissolution of four rock types was studied in dependence on time; the individual phases in the undissolved residue were identified by infrared spectrometry. The greatest difficulties were associated with the dissolution of garnet, tourmaline, andalusite, sillimanite, cyanite, staurolite, and hyperstene. Garnet and hyperstene are completely destroyed in 1 hr; the amount of other insoluble minerals decreases linearly with the logarithm of the reaction time. Andalusite can be dissolved after 5 hr, as can sillimanite and tourmaline; cyanite and staurolite remain undecomposed. Concentrated HNO_3 or H_2SO_4 accelerates the dissolution process, but polypropylene is damaged. Its decreased resistance to hydrogen peroxide in HF and H_2SO_4 solutions was described by Smith.[125] Polypropylene volumetric flasks are very suitable for storage of solutions containing HF (after sample decomposition).

Polycarbonate Erlenmeyer flasks are quite transparent, permitting observation of the whole decomposition process and thus decreasing the reaction time to a minimum.[77,81,84,161] The maximum permissible temperature is 130°C, but heating of the flask in a boiling water bath usually causes a complete decomposition.

As some Nb and Ta minerals are weakly attacked by HF (or HNO_3), Kallmann[162] recommends the use of a HF+HCl mixture under a slightly elevated pressure in a beaker covered with a tightly fitting polyethylene foil. Tantalite, columbite, pyrochlor, microlite, euxenite, and samarskite are dissolved, while zircon, cassiterite, and simpsonite remain undecomposed.

As documented by an increasing number of published works (especially since 1965), the problem of the development of a rapid and universal decomposition, enabling complete dissolution of mineral materials without respect to its phase composition, still exists. A number of reviews have been published[67,85,145,163-165] recently on this topic and a seminar was organized.[166] In order to achieve wider application of pressure decompositions in analytical practice, the present devices must be modified for series work, and PTFE distortion and metal autoclave corrosion during prolonged use must be decreased. Future development should concentrate on the following fields:

1. Introduction of new organic polymers which are resistive and have favorable properties at temperatures above 400°C. Although some such materials have found use in cosmic research and military technology, they have not yet been tested in analytical work. The use of noble metals apparently is not feasible, in view of their high cost and easy corrosion.
2. To date, changes in the redox conditions have been used minimally in pressure decompositions. Due to volume changes of polyvalent ions, the complete destruction of the crystal lattice of the mineral to be analyzed and its consequent dissolution may be attained more readily. The necessary reaction duration may be substantially decreased and complete mineral dissolution attained at a lower temperature. Structural factors (e.g., the location of the polyvalent ion in the crystal lattice, the formation and presence of vacancies, the structure of the product formed, and its behavior in the reaction mixture) can play a decisive role in this type of decomposition. The influence on the redox potential of some systems can help explain the dissolving effects of a $H_3PO_4 + H_2SO_4$ mixture on tourmaline; a lack of polyvalent cations may be one of the causes of the extreme resistivity of topaz and cyanite.
3. Thus far, the possibilities offered by closed system pressure decompositions for the determination of volatile components have not been fully utilized. This dissolution type is still almost exclusively employed for the determination of SiO_2, Hg, As, and occasionally for other components (e.g., B).
4. The treatment of the reaction solutions from the autoclave has not yet been reliably solved. When SiO_2, together with excess HF, must be removed from the solution prepared from higher sample weights (> 2 g alumosilicates and rocks), surface active products, decomposable with difficulty, are often formed. This probably prevents wider application of pressure decompositions in trace element determinations.

III. DECOMPOSITION IN OPEN SYSTEM

A. Decompositions by HF

Hydrofluoric acid occupies a special position among decomposition agents. It is a weak acid (pK = 2.9 in 0.5 *M* $NaClO_4$), and its effect as a solvent depends primarily on its complexing properties; it is the most pronounced of all hydrogen halide acids.[167] Fluoride has the smallest ionic radius (1.33Å) in comparison with other halides. It forms many series of very stable consecutive complexes, especially with polyvalent cations with a high electric charge density (e.g., Zr^{4+}, Ti^{4+}, Al^{3+}, Fe^{3+}, etc.), where, due to the favorable steric conditions, the number of ligands easily reaches the maximum coordination number.

Hydrofluoric acid is the only acid that reacts with silicon, silicon dioxide, and silicates, forming soluble H_2SiF_6 and leading to liberation of cationic components bound to the silicate lattice. When heated, H_2SiF_6 decomposes to gaseous SiF_4, and the solutions formed are free of silicon. The formation of fluoride and oxyfluoride complex anions facilitates dissolution of niobium, tantalum, and tungsten compounds and prevents precipitation of surface-active hydrolytic products in acidic solutions. However, reactions of some cations with fluorides yield sparingly soluble precipitates; this effect is utilized in separations of analyzed components. Procedures have been developed for separations of rare earth cations Th^{4+} and U^{4+} from other ions that form soluble complexes under identical conditions (e.g., Ta, Nb, and Ti). The fluorides formed at low concentrations are coprecipitated on separated insoluble calcium or lanthanum fluorides.

Although hydrofluoric acid does not cause valence changes during sample dissolution, it strongly affects the redox potential of the system by forming various stable complexes with the individual ions of the redox couple. The oxidized component usually forms more stable complexes. The reduced form of the given redox system is then readily oxidized by atmospheric oxygen, which causes negative errors (e.g., in the determination of Fe^{2+} in silicates after rock decomposition by HF).

Substances are usually dissolved in Pt crucibles or in plastic vessels. Common polyethylene vessels are used up to 70°C, linear polyethylene up to 120°C, and polypropylene or polycarbonate up to 130°C. A disadvantage of these plastic vessels is the poor stability of the polymers toward strong oxidants (hydrogen peroxide, aqua regia, etc.). Teflon is an ideal material as it can be used up to a temperature of 240°C and is stable even in solutions of strong oxidants. The fluorides formed can be decomposed by evaporation with perchloric or sulfuric acid directly in the Teflon dish. The reaction time is longer in plastic vessels, as these polymers have poor thermal conductivity. Therefore, devices for hastening the evaporation process have been proposed.[168]

In analytical laboratories, 38 to 40% HF is generally used; its composition is similar to that of the constantly boiling azeotropic mixture (38.26% HF, bp 112°C, p = 101·33 kPa). More concentrated acid, 48% HF, is also commercially available; it is prepared by introduction of gaseous HF into the azeotropic mixture. Very pure HF can now be prepared, utilizing new organic polymers in the construction of distillation apparatus and reaction vessels. The costly Pt devices originally used have been replaced by distillation instruments made of polyethylene,[169,270] polypropylene,[46] and Teflon. As the procedure employed often led to contamination of the distillate, ultrapure HF was successfully prepared by saturation of water with gaseous HF from a pressure cylinder.[171,172] The gaseous HF was purified by passage through a Teflon filter[173] and by freezing-out in a tank made from the Kel-F material. Isothermal and subboiling distillation[174-176] in which 48% HF is heated by a submersion element in a Teflon container and HF distills without boiling has also been used. This procedure enables the preparation of more concentrated HF (55 to 60%), which substantially shortens the reaction time required for dissolution of rock samples. Using 55 to 60% HF, rock pieces are completely dissolved in 1 day; the reaction time is 1 week using 48% HF. The efficiency of the separation of impurities was checked by adding ^{208}Pb; in optimum cases it is possible to obtain the acid with a lead content of less than 0.001 ng Pb^{2+} per gram HF. The efficiency of various techniques has been critically evaluated in a study by Arden and Gale.[54]

Dissolution of glass and quartz in HF solutions was first described by Scheele[177] in 1771 and by Bergman[178] at approximately the same time. This decomposition was introduced into the field of rock analysis by Berzelius.[179] The reaction proceeds at various rates, depending on the crystal lattice type of the given SiO_2-modification and on the grain size of the mineral analyzed. Both α- and β-quartz are dissolved rapidly enough even with a relatively large grain size (glass-making sands and fractions of very pure quartzes). The high-temperature modification crystoballite (obtained by ignition of silicic acid gel) reacts violently, especially with fine grain dispersion. Coesite and stishovite, polymorphous SiO_2 forms (formed by so-called shock metamorphism), do not dissolve in HF solutions; on the other hand, prolonged extraction of rocks in dilute HF and H_2SO_4 solutions is used for the separation of these rare minerals from quartz and other common rock-forming minerals.[180,181] Hydrofluoric acid alone is sometimes used for dissolution, but decompositions are carried out in mixture with strong acids (especially H_2SO_4, $HClO_4$, HCl, HNO_3, and aqua regia), which simultaneously destroy the crystal lattices of other accompanying nonsilicate rock minerals (pyrite, magnetite, calcite, etc). When the solution evaporates, a ternary azeotropic mixture of H_2O (54%) HF (10%) and H_2SiF_6 (36%) is formed. This mixture boils without changing composition, and the final solution is free of silicon. Because of the HF character (weak acid) and the formation of complex fluorosilicate as the reaction product, the reaction is slowed down by addition of a strong mineral acid.[43,182] The dissolution kinetics was followed in detail with quartz, staurolite, and epidote[43] in HF solutions and after addition of HCl, $HClO_4$, or H_2SO_4. The dissolution rate is most significantly decreased with quartz and epidote; there is no effect with staurolite. Alkali metal, alkaline earth, and heavy metal silicates, as well as minerals of the zeolite group, are very easily dissolved when treated with HF. Silicates with high aluminium contents (especially topaz and modifications of the Al_2SiO_5 compound) and with a lack of polyvalent cations are decomposed with difficulty.

To date, no relationship between the silicate structure and its solubility in HF has been found. Andalusite, sillimanite, disthene, zircon, staurolite, axinite, and tourmaline are very poorly soluble. The solubility of some minerals (especially garnets, some kinds of tourmaline, beryl, and lepidolith)[183] depends on changes in the isomorphous composition. This procedure has been employed for purification of monomineral zircon fractions[184] because zircon is resistant to HF + H_2SO_4 mixture, even at an elevated temperature of 240°C. The dissolved Zr^{4+} ion (3 to 5%) probably comes from the more easily decomposable ZrO_2 (baddeleyite) or, more likely, from a metamict conversion in the mineral surface. Feldspars and most micas, amphiboles, and pyroxenes are readily decomposed. In order to dissolve accompanying sulfides (especially pyrite), an effective oxidant must be added (e.g., HNO_3 or aqua regia). Chromite, occurring frequently in basic rocks, remains undecomposed, as does cassiterite in granite rocks. The resistivity of cassiterite toward HF was useful in studying differences between tin bound to this mineral and tin bound to silicates.[185] Analogously, chromite,[186] common spinel, chrysoberyl, rutil, corundum, and graphite or diamond can be isolated. These accessory minerals are concentrated in the undissolved rock fraction and can readily be identified microscopically or by X-ray and spectral analysis;[187] however, the original undissolved mineral phase must be differentiated from newly formed precipitates.[188] Dissolution of sediments in HCl and HF is utilized for the isolation of organic matter and microfossils;[189] however, about 30% of the organic component passes into solution.

Owing to the complexing properties of HF, the selection of analytical methods for the determination of the individual components is rather limited. For example, fluoride prevents quantitative separation of aluminium hydroxide, and its complex formation interferes with the spectrophotometric determination of many metal ions (e.g., Zr^{4+}, Ti^{4+}, Fe^{3+}, Al^{3+}, Be^{2+}, etc.). Fluoride is thus displaced from the reaction mixture by heating with another mineral acid, generally H_2SO_4, $HClO_4$, or H_3PO_4. So far it has been assumed[8] that addition of a strong acid prevents the formation of volatile fluorides (especially Ti^{4+} and Zr^{4+}) during evaporation. However, it is more probable that an apparent loss in these elements is caused by the masking effect of fluoride in the final determination method, rather than by the formation of volatile compounds. Removal of fluoride from the reaction mixture by repeated evaporation with a strong, poorly volatile mineral acid is tedious. Moreover, the data published in older works are not quite reliable, because sensitive methods for the determination of small fluoride amounts, especially in rock polycomponent materials, have been developed only recently. Fluoride displacement by H_2SO_4 is more efficient than by $HClO_4$, as a substantially higher reaction mixture temperature is attained during evaporation (200 to 250°C). After repeated evaporation, the fluoride is practically completely removed.[76,190,191] If the solution contains a larger amount of calcium salts (when H_2SO_4 is used), the fluoride displacement is not complete even after two evaporations; the fluoride remains adsorbed in the precipitated $CaSO_4$. The removal of fluoride is especially strongly hindered by the presence of excess Al^{3+} (Ti^{4+}, Zr^{4+}) in the use of both H_2SO_4 and $HClO_4$. It is sometimes recommended that H_3PO_4 be used for this purpose, but the most reliable procedure is fusion of the evaporation residue (after the decomposition of the rock material with HF) with $K_2S_2O_7$. Fluorides must be carefully removed in the determination of zirconium.[192,193] Oxalic acid has also been used for removal of fluoride; an excess can readily be decomposed by heating to 200 to 250°C, which produces carbonates which can easily be dissolved in acids.[194]

Evaporation of solutions with dissolved alumosilicates leads, especially with higher sample weights ($>$ 1 g), to the formation of sparingly soluble reaction products with high contents of aluminum and fluoride. These compounds are not completely decomposed even after multiple evaporation with $HClO_4$, H_2SO_4, or HCl. For example, in a German rock standard, slate TB, the insoluble fraction (after decomposition with HF, evaporation with $HClO_4$, and dissolution of the residue in HCl) consists mainly of a precipitated complex fluoride, while the fraction of resistant minerals actually present in the rock is small.[195] Langmyhr and Kringstad[196] chiefly identified compounds of the type Fe^{II} (Al_1 Fe^{III})$F_5\cdot xH_2O$, $NaAlF_4\cdot xH_2O$ and $MgAlF_5\cdot xH_2O$ in the isolated fraction; these substances were mostly obtained by dissolving pure oxides or carbonates in HF. Precipitates obtained in common dissolution procedures with rocks have more complicated compositions, determined by the initial composition of the analyzed rock and by the decomposition conditions.[195-197]

In the decomposition of the mentioned standard slate TB with a defined phase composition, a substance structurally close to rare mineral ralstonite, $Na(Mg, Al)_6[F, OH]_{18}\cdot 3H_2O$, was isolated from the residue after evaporation with HF and $HClO_4$. The distribution of the individual elements, particularly F, Al, Fe, Mg, Ti, and Na, was studied in this precipitate using an X-ray microanalyzer;[195] only negligible amounts of the original undecomposed phases were present (virtually only rutil and tourmaline). Chemical analysis yielded fluoride contents of up to 48% and aluminum contents of up to 20%; other major components included Fe, Mg, Na, and K. In order to dissolve these precipitates, concentrated solutions of beryllium and aluminum salts are employed,[76,198] as they react with the precipitate to give simpler soluble fluoride complexes. The most frequently used, but less effective, reagent is boric acid. One disadvantage of these dissolution procedures is the introduction of another compound into the solution, which makes some determinations more difficult or prevents them (e.g., Al). Difficulties are also encountered in the AAS determination of low concentrations of alkaline earths in the presence of extreme excesses of Al. Here the addition of H_3BO_3 is more advantageous. Beryllium aerosols are very toxic. However, precipitates formed during the decomposition or during solution evaporation to a small volume or to dryness (sometimes after evaporation of the residue with $HClO_4$ and dissolution in dilute HCl) could not be completely dissolved by this procedure. Insoluble reaction products are also formed even with small sample weights and are usually imperceptible in solutions due to the very fine precipitate dispersion. With higher sample weights ($>$1 g), variable amounts of reaction products are often formed; this fraction varies irreproducibly between 0.5 and 7% with the above standard slate.[195] When a larger amount of rock is employed for the analysis, the concentrations of the reactants are markedly increased toward the end of the decomposition, thus, compounds unusual in both type and structure are precipitated. Their identification is difficult, as the appropriate X-ray structural data are lacking. Some data on the solubility of certain simple compounds were given by Langmyhr et al.;[199] the $MgAlF_5$ compound, obtained by precipitation in solutions containing Al^{3+} and Mg^{2+}, is least soluble (Table 1).

The formation of insoluble compounds during the decomposition complicates the determination of Ca in kaoline; the complex fluoride separated, containing adsorbed Ca^{2+} ions, is not completely dissolved even by prolonged evaporation with $HClO_4$. The determination of traces of Ba^{2+} is subject to similar difficulties;[200] among 14 analyzed rocks, the insoluble residue contained more than 20% of the Ba present in seven cases, even if the rocks analyzed did not contain resistant baryte. This problem can be partially solved by

TABLE 1

The Solution Composition in the Analysis of Slate Tonschieffer TB

Ion	Concentration (mol/l)
Na^+	1.7
K^+	3.3
Ca^{2+}	0.2
Mg^{2+}	1.9
Mn^{2+}	0.03
Al^{3+}	16.1
Fe^{3+}	3.5
PO_4^{3-}	0.05

Note: Standard rock from ZGI Berlin; the concentrations given above are obtained after dissolution of 2 g of the rock and solution evaporation to 0.5 ml.

AAS determination using a low-weight sample in an HF solution without preliminary removal of SiO_2; a small amount of a precipitate can be dissolved by adding H_3BO_3. The fluoroborates formed decrease mutual interferences in the determination of major rock components by AAS.[57] Another reliable procedure is isolation of the precipitate by filtration and its transfer into solution by fusion (with lithium borate, B_2O_3, Cs_2CO_3 or $Cs_2S_2O_7$) and dissolution of the melt in a strong acid. For decomposition of these sparingly soluble fluorides, treatment with 6 *N* HCl at 120 to 180°C in a closed system under pressure has been recommended.[54] Difficulties are encountered, especially in the determination of high concentrations of potassium. The precipitate formed, containing complex fluorides,[201] retains substantial amounts of potassium and is usually enriched in potassium compared to the originally analyzed mineral. The precipitate slowly dissolves in 1 *M* HCl and the final AAS determination of potassium is carried out after standing in a diluted solution for 24 to 72 hr. After ignition of the residue obtained by evaporation of the sample with HF and $HClO_4$, thermal decomposition of perchlorates occurs, alkali metal salts are converted into the chlorides, and alkaline earth salts are decomposed to a mixture of chlorides and oxides. At 500 to 550°C ferric and aluminum perchlorates are converted into the corresponding oxides. Alkali metal chlorides[202] are isolated by extraction of the ignited residue with water, and $SrCl_2$ is separated from excess aluminum[203] by treatment with very dilute HCl.

Iron and aluminum sulfates formed during the decomposition are thermally decomposed, forming oxides, from which alkali metal sulfates can be extracted with water.[204-206] However, alkaline earth sulfates are thermally stable under these conditions. The extraction of K^+ and Li^+ is not complete,[207-209] as they are absorbed by ignited Al_2O_3. These procedures have been superseded by flame spectrometric methods for direct determination of the alkali metals without separation.

Polyvalent elements are present in various valence states in crystal lattices of solid substances. On dissolution they can be reduced or oxidized; sometimes they react with the solvent, are oxidized by atmospheric oxygen, or the ions formed react together. In inorganic analysis these problems are encountered particularly in analyses of ferrites and in the determination of Fe^{2+} in various materials (e.g., glass and rocks).[210] In lunar rocks, lower valence states of other elements must also be determined, e.g., Ti^{3+} and Cr^{2+}. Thus, a successful determination depends not only on complete dissolution of the analyzed substance, but also on the maintenance of the given ion in the original valence state. Errors may have been committed in the initial stage of sample preparation. Fine powdering of a mineral in the presence of air causes rapid oxidation of the FeO present, which is the most important cause of errors in determinations, especially with hard minerals requiring prolonged powdering for preparation of the analytical sample. Certain garnets (especially almandine), pyroxenes, and amphiboles are oxidized very rapidly. Therefore, it is recommended that the final fine analytical sample be prepared by pulverizing small pieces under acetone or ethanol or in an inert gas atmosphere.

The results obtained were improved by using Teflon vessels for the decomposition; an inert atmosphere can also be maintained perfectly. Transparent polypropylene bottles with screw caps[211] or polycarbonate flasks[39,77] in which the whole dissolution process can be watched are also suitable. The dissolution is best carried out in a boiling water bath.

Undesirable chemical reactions frequently occur in the solutions obtained, leading to oxidation of Fe^{2+} or reduction of Fe^{3+}. Higher oxides of manganese exhibit oxidizing effects.

Organic matter and certain other as yet unidentified rock components always present in rocks of sedimentary origin have reducing properties.[212];[213] Graphite does not react with the Fe^{3+} present. The reducing properties of some components (sulfides including pyrite and organic materials) are especially pronounced if the decomposition proceeds in the presence of excess oxidant. Metallic iron[214] also has strong reducing properties (from abrasion of homogenization devices).

The FeO concentration is usually determined by oxidimetric titration or the excess oxidant is back-titrated with a reductant (the Mohr salt). Usually, only easily decomposable minerals are dissolved directly in HF and H_2SO_4. If a mineral decomposes very slowly, it is dissolved in the presence of excess vanadate, bichromate, or permanganate. It is then unnecessary to maintain an inert atmosphere during dissolution, as Fe^{2+} ions liberated are immediately oxidized to Fe^{3+}; complete decomposition by HF and an oxidant is sometimes achieved at laboratory temperature. As the fluoride complexes of tervalent iron are much more stable than those of divalent iron, the formal redox potential of the Fe^{3+}/Fe^{2+} system considerably decreases. Therefore, Fe^{2+} ions are very easily oxidized in HF solutions and an inert atmosphere must be very carefully maintained during dissolution. Before titration, the fluoride is bound by adding boric acid, which dissolves complex fluoride precipitates which can contain Fe^{2+}. In spectrophotometric determination of FeO, a reagent that reacts only with Fe^{2+} is used; the sample is dissolved most frequently in the presence of phenanthroline or a triazine derivative.[109,216]

This direct method of determining FeO is not suitable for resistant materials. The behavior of garnets and glaucophanes[217] in HF solutions depends on their chemical composition. Among micas, flogopite is dissolved most slowly; alkaline amphiboles and pyroxenes require prolonged treatment with HF and H_2SO_4 for complete decomposition. Siderite[218] is slowly dissolved in this medium, which is uncommon among carbonates. Rutil, corundum, cassiterite, spinel, and chromite remain completely undecomposed.

Vanadate is most suitable for decompositions in the presence of excess oxidant; dichromate is also used often, while permanganate[219] is only occasionally used. When employing common sample weights (0.2 to 0.5 g), 10 ml HF and 0.1 g vanadate (as a solution acidified with H_2SO_4) are added. The reaction is allowed to proceed in a Teflon dish, preferably overnight without heating. Excess oxidant is back-titrated with a ferrous salt using diphenylamine indicator. Sulfides (including pyrite) and organic materials interfere. This method was successfully applied to the determination of FeO in rocks,[220-223] ashes,[224] and mineral allanite.[225] Heating of silicates in solutions containing HF, H_2SO_4, and $K_2Cr_2O_7$ in order to determine FeO was proposed by Hackl[226] as early as 1925. When small amounts of Fe^{3+} are present in the analyzed solution, dichromate is spontaneously reduced; the cause of this reduction in HF solutions has not yet been unambiguously clarified.[227] This undesirable reaction is strongly suppressed by addition of a ferric salt,[227-229] so that the FeO can then be determined in some garnets, augite, epidote, glaucophane, and other minerals. The two procedures were critically evaluated[230] and the vanadate procedure was found to be better. Permanganate, which is also used occasionally is poorly stable in HF solutions.[231]

Divalent iron can also be determined after oxidation with ICl in a medium of HF and HCl;[232] the iodine liberated according to the reaction

$$2ICl + 2Fe^{2+} \rightarrow I_2 + 2Cl^- + 2Fe^{3+}$$

is determined by titration with iodate (in the presence of CCl_4) or with thiosulfate. Obsidian and plagioclase are dissolved within 1 to 2 min in solutions of HF, HCl, and ICl in a Pt dish,[233] while pyrite is not attacked to a greater extent. Nichols[234] modified this procedure for sedimentary rocks with organic components. The rock decomposition can be visually followed in a centrifugation test tube[235] made of an ethylene-tetrafluoroethylene polymer (Tefzel® from the Nalge Company[39]). Oxidation with ICl was also employed in the determination of Fe^{2+}, Cu^+, metallic copper, and arsenite in glasses.[236-239]

Iodate is reduced to iodine by Fe^{2+} in a HF and H_2SO_4 medium; the iodine is removed by boiling the reaction mixture:

$$10Fe^{2+} + 2IO_3^- + 12H^+ \rightarrow 10Fe^{3+} + I_2 + 6H_2O$$

Excess iodate is titrated with thiosulfate. This method was employed for the determination of FeO in standard G-1 and W-1 rocks.[240]

The decrease in the redox potential of the Fe^{3+}/Fe^{2+} system due to the presence of fluoride enables selective oxidation of $FeF_6{}^{4-}$ ions by a silver salt:[241]

$$FeF_6{}^{4-} + Ag^+ \rightarrow FeF_6{}^{3-} + Ag^0$$

Excess Ag^+ is titrated with bromide. This procedure has been successful in practice especially in the determination of FeO in the presence of organic substances and small amounts of sulfides.

The precision of the FeO determination depends not only on the presence of interferants, but also on the Fe(III)/Fe(II) ratio in the analyzed material. Therefore, Fe_2O_3 is sometimes determined directly (e.g., by titration with a mercurous salt,[242] ferrocene,[243] EDTA,[244] or coulometrically[213] by generated Ti^{3+}).

Hydrofluoric acid is a very important solvent for titanium ores. It decomposes the silicates present and hastens the dissolution process by formation of stable fluoride complexes. The solutions thus obtained do not hydrolyze; consequently, this procedure has found use in analyses of niobates and tantalates with high titanium contents. The material is usually dissolved in HF in the presence of another acid, especially sulfuric or perchloric. In order to ensure complete material dissolution, the decomposition is terminated by fusion with $KHSO_4$. Among titanium oxides, rutil does not dissolve in HF even under elevated pressure; on the other hand, anatase is readily dissolved in the above acid mixture. Ilmenite and loparite are decomposed analogously, as is titanite.[245-248] Generally, in combination with HF, $HClO_4$ is less effective as a dissolution agent than H_2SO_4, with which the reaction mixture temperature can further be increased by adding an alkali sulfate that also serves as a fusion agent in the terminal stage of the decomposition. Perovskite structure minerals are dissolved with difficulty, and the entire process must be repeated many times.[249] Dissolution of large samples (up to 30 g) of Ti ores is a very difficult analytical task; in spite of this fact, many very effective procedures have been developed (e.g., for the determination of traces of platinum metals in titanomagnetites or kimberlites).[250] Samples with excess Ca^{2+} are dissolved in a HF and HCl mixture. The individual decomposition stages must be repeated several times and the isolated resistant fraction fused with $KHSO_4$ or Na_2O_2.

Decomposition with HF is also one of the few reliable procedures for obtaining a stable solution after dissolution of Nb and Ta minerals; it is used with both poor ores and concentrates. The dissolution is facilitated by the formation of complex anions, $(TaF_7)^{2-}$ or $(NbF_7)^{2-}$. A decrease in the HF concentration is accompanied by conversion of the niobium complex[251] into an oxyfluoride complex $(NbOF_5)^{2-}$; this effect was analytically utilized (e.g., in the extraction separation of the two similar elements). The decomposition of Nb (Ta) minerals by HF was introduced into analytical practice as early as 1883 by Smith[252] in the analysis of samarskite. Minerals with niobium predominating are decomposed more easily; the decomposition is usually terminated by fusion with $KHSO_4$. In analyses of polycomponent ores (e.g., containing cassiterite and zircon), dissolution in HF is sometimes combined with acidic ($KHSO_4$) and alkaline (Na_2CO_3-sodium tetraborate or Na_2O_2) fusion of the undissolved fraction.[253] Microlite is almost completely dissolved in dilute HF at laboratory temperature,[254] but columbite reacts more slowly. Pyrochlor is also dissolved;[255] when a high concentration of iron is present, the ore is first extracted with diluted HCl, in which this mineral is virtually insoluble. Brazilian ores containing barium niobate (pandaite) are extracted with a mixture of HF and HCl, which yields more reliable results than direct fusion with $KHSO_4$ and dissolution of the melt in tartaric acid.[256-257] During dissolution of Nb (Ta) minerals in HF, a precipitate of thorium(IV) and uranium(IV) fluorides is formed; it has been experimentally verified that the precipitate also contains hexavalent uranium.[258] If the composition of the analyzed ore is not known exactly, the whole sample must be dissolved prior to analysis by combining various decomposition procedures. The specialized literature often contains contradictory data concerning the decomposability of various Nb-Ta minerals, which can be explained by changes in solubility due to mutual isomorphous displacement between Nb and Ta, as well as by variability of the concentrations of other mutually exchanging components.

Decomposition with HF combined with HNO_3, H_2SO_4, or $HClO_4$ belongs among standard procedures employed in analytical evaluation of uranium and thorium ores. These procedures are particularly useful when the ore-bearing mineral is finely included in silicate rocks. The chief industrially important uranium ore minerals (e.g., pitchblende, uranium micas, uranium blacks) are readily dissolved in this way; tetravalent uranium is oxidized to hexavalency during the dissolution. Thorium minerals (e.g., monazite), are more difficult to decompose. However, for geochemical purposes, it is often necessary to determine even trace contents of the two elements (of the order of units or tenths of parts per million); the whole analyzed rock sample is then dissolved, usually combining several very effective decomposition techniques in order to decompose resistant minerals containing U and Th, such as zircon. After decomposition with HF, the residue is isolated and fused with sodium carbonate and tetraborate or with B_2O_3 or it is sintered with Na_2O_2.[259,260] With basic rocks and sediments with a high concentration of $CaCO_3$, formation of $CaSO_4$ during the decomposition should be avoided, as it may retain thorium.

The low solubility of uranium(IV), thorium, and rare earth fluorides is often utilized in analytical practice for group separation of these components. As the precipitates formed are frequently colloidal and present difficulties in filtration, a calcium salt is added. The CaF_2 precipitated forms isomorphous compounds with UF_4 and serves as a collector.[261-263] However, the precipitate is often contaminated with Fe, Al, Zr, and Ti salts, which form binary fluorides with Ca^{2+}.

Combinations of decomposition agents (HF, HNO_3, HCl) have proven effective in treatments of large soil samples for determinations of certain transuranium elements.[264] Plutonium is isolated from the final nitrate solution by anion exchange. The efficiency of the procedure equals 53 to 60% of the overall Pu content, compared with the results obtained after sample decomposition by fusion with Na_2CO_3. Of tungsten minerals, scheelite, wolframite, and tungstite dissolve in HF solutions; tungstate is extracted using potassium hydroxide from the evaporation residue.[265]

Under strictly defined reaction conditions the solution obtained after dissolution of SiO_2 by HF can be heated in a water bath without volatilization of SiF_4. This can be explained on the basis of the ternary diagram for the H_2O, HF, and H_2SiF_6 system: Close to the region of azeotropic mixture of HF and H_2O, the liquid ternary mixture is in equilibrium with a gaseous phase in which the H_2SiF_6 concentration is much lower than in the liquid.[76,266] When solutions containing H_2SiF_6 are evaporated at laboratory temperature or heated to 60°C and the liquid volume is not decreased substantially, losses in SiO_2 are negligible. Even at a temperature of 100°C there is no perceptible volatilization of H_2SiF_6 in the initial stages of evaporation.[267] After evaporating to a small volume, the composition of the liquid phase becomes identical to that of the constant-boiling ternary mixture of $HF\text{-}H_2SiF_6\text{-}H_2O$; H_2SiF_6 quickly escapes from the solution. This provides the necessary theoretical conditions for the determination of SiO_2 after dissolution in HF (e.g., in iron ores[268,269] and fluorites[159]).

Fluorides of a number of other elements are also volatile; the melting and boiling points for some compounds are given in Table 2. These values[270] often are not in accordance with knowledge gained during long analytical studies. In reactions of HF with solid phases, volatile fluorides of the above-given composition are not formed under the decomposition conditions. The overall reaction is further complicated by side reactions, giving rise to nonvolatile complex fluoride anions (with the maximum coordination number in the presence of excess HF) and to the formation of oxyfluorides and other hydrolytic products. Substantially larger losses in the form of volatile fluorides have been observed with As(III) than with As(V); Se(IV) and Te(IV) behave analogously in comparison with Se(VI) and Te(VI). According to Table 2, fluorides of higher valence states are much more volatile; however, they are probably not formed in the reaction

TABLE 2

The Melting and Boiling Points of Some Fluorides

Compound	Melting point (°C)	Boiling point (°C)
BF_3	−128	−100
GeF_4	–	-37^a
SiF_4	–	-95^a
SnF_4	450	705
TiF_4	–	284
ZrF_4	–	900
AsF_3	−8.5	63
AsF_5	−79.8	−52.8
SbF_3	292	376
SbF_5	7	150
NbF_5	72	236

[a]Sublimation.

mixture during decompositions with HF or immediately undergo hydrolytic reactions. On the other hand, experimental results indicate that fluorides of lower valence states are formed rapidly and cause great losses in some elements through volatilization, e.g., As(III). Contradictory data on the volatility of various components frequently appear in the literature. Apparent losses may be due to the masking effect of fluoride in the determination of the element or to formation of insoluble films irreversibly adsorbed on the vessel walls, etc. The data concerning volatilization of As from HF solutions are often very variable. Most authors[271,272] agree that As(III) volatilizes as AsF_3; during evaporation of solutions to H_2SO_4 fumes, losses of up to 45% were detected using the ^{74}As radioisotope. Heating of As compounds in an oxidizing mixture of HNO_3-$HClO_4$-HF leads to complete volatilization[273-275] of As. However, this decomposition technique was used for the determination of microgram amounts of As in silicate rocks and minerals without observing losses[276] of As. During cautious evaporation of As(III) salt solutions with HNO_3 and HF, losses[273] in As of up to 30% have been detected using ^{74}As; this is in accordance with data given by Ploum.[277] Nevertheless, this solution preparation is employed in the analyses of sulfidic ores.[278] No losses in As have been observed[279] in the analysis of silicates after material dissolution in HF and HNO_3 and oxidation with $KMnO_4$. This oxidizing mixture has been recommended for the decomposition of glasses[280] (the determination of total arsenic); AsF_3 volatilizes after treatment with HF, and As(V) remaining in solution can be determined. The content of the individual valence states of arsenic can be found from the difference between the two determinations. As the data given for the As volatility are quite contradictory for certain decomposition procedures, it is necessary to assume further interaction with the components of the dissolved material. In contrast to arsenic, antimony compounds do not volatilize when treated with HF and H_2SO_4 mixture even if the solutions are evaporated to the appearance of dense SO_3 fumes. No losses have been observed, even with trace concentrations[281] or in the analysis of raw Sb_2O_3.[282] During evaporation of solutions with a HF and $HClO_4$ mixture, the losses amounted to 10%. Addition of HNO_3 causes a decrease in these losses similar to that caused by As.[273,275]

Evaporation of solutions containing HF, H_2SO_4, and ^{119}Sn causes considerable losses in Sn (up to 25%).[125] In view of the high boiling point of SnF_4, this loss cannot be explained by the formation of volatile SnF_4.

Because of the exceptionally high volatility of BF_3, the materials for the determination of boron (quartz, silicon, silicates) must be dissolved very cautiously, preferably at a temperature of 20°C in a plastic vessel.[283,284] Nonvolatile fluoroboric acid is formed by the reaction between borates and HF; it then reacts with basic dyes giving rise to a colored associate extractable into organic solvents. Other components, e.g., the TaF_7^{2-} anion, react analogously. In the determination of tantalum, the interfering boron is removed from the solution by a suitable modification of the dissolution conditions,[285] so that BF_3 quantitatively escapes. All the boron is also lost after evaporation of an HF solution with $HClO_4$. The formation of BF_3 is prevented by adding mannitol. The mannito-boric acid formed does not volatilize even during evaporation of solutions to a smaller volume;[286,287] the procedure has been used in the analysis of quartz and quartz glass. The effect of H_3PO_4, which binds boron and prevents its volatilization,[288] is noteworthy. The solutions are evaporated after addition of H_3PO_4 and SiF_4 volatilizes completely. In the terminal stage, the reaction mixture can be heated up to 150°C without formation of BF_3. Dissolution of soils in HF and H_2SO_4 was recommended in geochemical prospection for colemanite.[289] However, standard G-1 and W-1 rocks do not release boron completely when treated with HF at laboratory temperature.

The accuracy of the determination of traces of Ge in rocks depends strongly on the method of preparation and dissolution of the analyzed material. The use of HF cannot be avoided, as Ge(IV) is isomorphous with Si(IV) and is built into the crystal lattices of silicate materials. Sulfides may also contain Ge(II); thus, the decomposition must be oxidative. In the analysis of coal ashes, considerable losses in Ge occur during the combustion process. A mixture of HF with HNO_3 and H_2SO_4 is usually employed for silicate dissolution, but more reliable results are obtained using H_3PO_4 as an acid of low volatility,[290-294] instead of H_2SO_4. Adding potassium phosphate is also very effective. Reactions taking place between germanic (boric) and phosphoric acids are not sufficiently understood; in view of the similarity between germanic and boric acids, their reactions will be of the same type. With boric acid, BPO_4 is probably formed.[295]

Substantial amounts of Se(IV) volatilize during evaporation,[296] even if the temperature is not high. The losses increase when the temperature of the reaction mixture is increased during evaporation with HF, HNO_3, and $HClO_4$; microgram amounts of Se can escape completely.[274,275] In the decomposition of deep sea sediments labeled with ^{75}Se, Se(IV) fluoride does not volatilize[297] in solutions of HF and HNO_3. Therefore, included selenide impregnations in sulfidic ores can be oxidized and converted into selenites in this manner. Using the same isotope, the decomposition technique was later verified[298] for the determination of trace amounts of Se. The experimental procedures proposed mainly employ this decomposition;[299,300] sometimes the solution formed is heated until the appearance of $HClO_4$ fumes, without observing losses in Se.[301,302] Chromium seriously volatilizes in this solution, probably as the oxyfluoride CrO_2F_2; microgram amounts can be lost completely. However, analyses of standard rocks have shown that the loss in Cr is negligible with small amounts of $HClO_4$ at the minimum evaporation temperature.[303]

The loss of tellurium compounds is small compared to that of selenium. Bock[304] studied the behavior of Te during decompositions in detail; he reports a maximum loss of 5.4 and 7.3% (when glass is dissolved in HF and H_2SO_4, respectively). When H_2SO_4 is replaced by aqua regia, no loss of Te occurs.[115]

When the reaction mixture temperature is increased during removal of fluoride (by adding $HClO_4$ or H_2SO_4), a loss in Re[305] is encountered. No loss in Re (1 μg) was observed when a solution of HF alone was evaporated. Losses of 4.7 to 7.6% have been reported for 50- to 100-mg samples; the amount of Re volatilized decreases to 1% following the addition of H_3PO_4.[306]

It is difficult to dissolve a sample without losing part of the markedly volatile Tl compounds. Radiochemical testing with ^{204}Tl has indicated that up to 40% of the total amount of Tl can be lost during prolonged evaporation with HF and $HClO_4$ or H_2SO_4. Reproducible results were achieved[307-309] after rock material dissolution in HF and HNO_3 and removal of the fluoride by evaporation with the latter acid.[307,310] No loss in Tl has been observed[311] after cautious dissolution in HF and solution evaporation with $HClO_4$. Thallium compounds do not volatilize when solutions containing HF, HNO_3, and H_3PO_4 are evaporated to a syrupy consistency.[312]

Radioisotopes were employed to monitor losses in Rb and Cs during silicate destruction[313] by HF and $HClO_4$; the losses amounted to 0.2 to 0.3% in closed vessels and to 1.3 to 1.4% in open crucibles.

The product of the reaction between H_3BO_3 and HF is fluoroboric acid, which is also sometimes employed for dissolving inorganic materials. HBF_4 formation is catalyzed by H^+ ions; acids of the $HBF_{4-n}(OH)_n$ type are formed as intermediates.[283,284] The hydrolytic process

$$HBF_4 + n\,H_2O \rightleftharpoons HBF_{4-n}(OH)_n + n\,HF$$

proceeds in the opposite direction.

HBF_4 is a selective solvent for silicates;[314] while quartz remains unattacked (the determination of free SiO_2). Among silicates[315] with isolated tetrahedrons, hessonite and almandine are partly attacked, while cordierite is dissolved smoothly. Micas, some amphiboles, and (among clay materials) kaolinite and illite are decomposed. The solubility of plagioclases decreases with increasing basicity. Magnetite reacts very rapidly, while pyrite is damaged very little. HBF_4 dissolves zeolites[316] at laboratory temperature; the solution obtained was used for X-ray spectral analysis. Lead alloys[317] are dissolved within 30 sec in this acid. Objective evaluation of the decomposition effects of HBF_4 is complicated by the complex decomposition kinetics and by the effect of hydrolytically liberated HF.

The decomposition technique using HF vapors (rarely used) meets even exceptionally high demands on the blank value.[318] The gaseous phase formed by vaporization of specially pure acids contains a minimum amount of impurities. This decomposition technique has been especially used in the analysis of quartzes, quartz glass, and silicon.[319,320] Even large grain materials can be dissolved in a special Teflon apparatus.[321] Decompositions with dry HF have been reviewed in the above-cited study.[270]

B. Decompositions by Other Volatile Inorganic Acids

1. Decomposition by HCl

Hydrochloric acid is the most frequently used reagent in decompositions of inorganic materials.

It is employed both for direct dissolution of the analyzed solid phase and for conversion of melts into soluble salts. Its effect as a strong acid is hastened by its pronounced complex-forming ability (especially with the transition elements) with stepwise formation of chloride complexes which are often intensely colored (e.g., those with Fe^{3+} and Co^{2+}). These reactions are utilized in analytical chemistry in ion-exchange chromatography and in extraction separations of complex mixtures, especially with oxonium solvents and long-chain amines.

Hydrochloric acid exhibits slight reducing properties as a solvent, manifested by reduction of higher oxides of manganese. However, hydrochloric acid is mostly used in mixtures with other inorganic acids, especially HNO_3; highly efficient oxidizing mixtures (aqua regia and the Lefort modification of aqua regia) result from this combination.

Hydrochloric acid has enjoyed extensive use in the analysis of natural and synthetic carbonates. Calcite and heavy metal carbonates react most rapidly and are decomposed at normal temperature even by very dilute HCl solutions. On the other hand, siderite and magnesite react slowly in hot 6 to 12 *N* HCl. The solubility of magnesite depends on the conditions of its formation. Magnesites of metasometic origin are decomposed slowly, while the same minerals bound to serpentine bodies are dissolved approximately twice as rapidly. The different reaction rates cannot be ascribed to different structures as X-ray diffraction data and IR spectra of the two magnesite types are identical.[322] The solubility of oxides varies according to the temperatures to which the analyzed substances were exposed and the rate of back-hydration. The specific surface of solid phases is decreased by high temperatures, and the crystal lattice is often reorganized. Both of these processes are connected with a decrease in the substance reactivity with mineral acids, especially HCl. Hydration reactions lead to formation of H_2O molecules or OH-groups in the mineral structure, causing an increase in the mineral reactivity. With complex iron oxides, components with higher concentrations of the hydrates oxides or Fe(II) react more rapidly with HCl. For example, hydrated ferric oxide (limonite) and ferrous–ferric oxide (magnetite) react faster than two anhydrous forms of Fe_2O_3 (hematite and specularite). On the other hand, the solubility of pitchblende (U_3O_8) decreases with increasing contents of U(IV). Hydration products of Al_2O_3 behave analogously, but their solubility in HCl is substantially lower ($AlCl_3$, poorly soluble in HCl, is probably formed at the liquid-mineral interface). Anhydrous α-Al_2O_3 (corundum) is virtually insoluble in this acid. Quartz and cassiterite are insoluble and only some colloidal forms of natural Sn(IV) oxides are soluble. Rutil behaves similarly, while another TiO_2 modification, anatase, is quite soluble. Natural and synthetic MnO_2 is decomposed, producing Cl_2; the dissolution process is hastened by H_2O_2, which acts as a reductant.

Synthetic substances are generally more readily soluble in HCl than minerals of the same chemical composition. Freshly precipitated $PbSO_4$ smoothly dissolves in 6 *N* HCl with formation of chloride complexes, while mineral anglesite of the same composition is not dissolved completely even in concentrated HCl or aqua regia. After ignition, the PbO formed dissolves in the acid; however, some ore minerals react with the silicates present during ignition and form resistant compounds, from which metallic components (Cu) can be extracted only after total destruction of the silicate lattice by HF. Hydrated calcium sulfate (gypsum) is decomposed easily by HCl, but anhydrous anhydrite is dissolved slowly and incompletely. Baryte is not attacked to a perceptible extent, and coelestine is decomposed only to 5 to 10% in HCl (1+1), depending on the decomposition conditions.

Apatite reacts very rapidly,[323-325] as do heavy metal phosphates and phosphates of the type R(II) $(UO_2)_2(PO_4)_2 \cdot x\ H_2O$, which belong among uranium micas. Rare earth and thorium phosphate (monazite and xenotime) are dissolved incompletely.

Tungsten ores, containing chiefly wolframite or scheelite, are decomposed in HCl, yielding insoluble tungstic acids. Various modifications of this decomposition procedure are used to separate tungsten from accompanying components. However, molybdenum is not separated in this way.

Among borates, industrially important mineral colemanite is readily dissolved in HCl; the decomposition is carried out in a quartz glass vessel under reflux, because of the volatility of H_3BO_3. Fluorite is dissolved slowly in HCl, and the dissolution is hastened by addition of aluminium salts or H_3BO_3.[326]

Pyrite reacts to a negligible degree, depending on the solution composition and probably also on genetic factors.[327] Galenite is dissolved within 10 min in diluted HCl (1+1); Ag^+, Bi^{3+}, and Tl^+ are adsorbed by $PbCl_2$ precipitated during cooling.[328,329] For trace amounts of silver, 3 *M* HCl suffices for dissolution of AgCl (in the form of $AgCl_2^-$), but 8 *M* HCl is necessary for conversion of precipitated $PbCl_2$ to soluble chloride complexes.[330] High acidity of the analyzed solution can be avoided by adding diethylene triamine,[331,332] which forms stable complexes with Pb^{2+} and Ag^+ even at pH 1. Other industrially important sulfides, antimonite, and sphalerite are also dissolved. An oxidant is added to prevent formation of volatile $SbCl_3$; however, complex anions $[SbCl_6]^-$ tend to hydrolyze even in 6 *M* HCl. Volatilization of $AsCl_3$ is prevented by oxidation of As(III) to pentavalency.

Decomposition of sulfidic ores is hastened by addition of oxidants, especially HNO_3, Br_2, H_2O_2, or $KClO_3$.[333] A strongly oxidizing mixture of Cl_2 and ClO_2 is produced from $KClO_3$ depending on the reaction conditions. When the analyzed substance is heated in an HCl solution, H_2S is first displaced, and the decomposition is then completed by added oxidant. In this way, the formation of sparingly soluble $PbSO_4$ is suppressed. $KClO_3$ is used when the presence of HNO_3 interferes in the final analytical procedure. This procedure ensures complete dissolution of cinnabar, pyrite, molybdenite, Ni and Co arsenides and sulfoarsenides, arsenopyrite, and other sulfidic minerals.

Heavy metal silicates and minerals of the zeolite group release silicic acid gel when treated with HCl. The gel has strong adsorptive properties; structurally it retains the form of the original mineral,[334] but the cations are replaced by H_3O^+ ions. Heulandite, desmine, chabasite, analcime, and other zeolites react in this way. However, most rock-forming silicates are resistant and are only partially damaged by HCl.

Graphite and organic materials are often separated from carbonates by dissolution in HCl. However, because of the variable character of organic substances in sedimentary rocks, this procedure may lead to gross errors in the determination of organic carbon,[335-339] as some organic compounds (especially those containing nitrogen) dissolve in HCl; the losses amount to 30 to 50% of the total nitrogen.

During dissolution, compounds of As(III), Sb(III), and Sn(IV) volatilize, and losses in In (up to 18%) are encountered. Volatilization of $InCl_3$ is eliminated by addition of KCl.[340] An analogous effect is exhibited by $ZnCl_2$ which is formed by the dissolution of zinc ores, preventing losses in Hg in the form of $HgCl_2$.[341] Selenium(IV) forms a volatile oxychloride[297] with HCl, while tellurium(IV) does not volatilize under identical conditions.[304] $GeCl_4$ volatilizes[342] even at 20°C from 8 *M* HCl.

2. Decomposition by HBr

HBr is used less frequently than HCl for dissolution of inorganic materials. The effect of HBr is increased by addition of bromate or HNO_3. Free bromine is liberated from HBr solutions by the oxidizing effect of HNO_3; the mixture energetically oxidizes the solid phase, similar to aqua regia.

HBr alone is an excellent solvent for magnetite.[213] Sulfides are readily dissolved when HBr is combined with the above oxidants. Pyrite, sphalerite, and tetrahedrite are rapidly dissolved, and arsenides, sulfoarsenides, and selenides are also oxidized. This oxidizing mixture readily dissolves tellurium minerals.[343-345] Gold is completely extracted from rock samples, as has been verified using radioisotopes.[344,346,347] The bromide complexes of Au(III) obtained are extracted into methylisobutylketone and are determined by AAS. Platinum and palladium are extracted under the same conditions.[348]

On heating of solutions with HBr and $HClO_4$, bromides of As(V), Sb(V), and Sn(IV) volatilize; this procedure was employed for separation of these elements in the analysis of lead ores.[349-351] A high evaporation temperature may also lead to losses in indium; however, volatilization is prevented by adding KCl. Tellurium does not volatilize during evaporation of HBr solutions.[304]

Elemental bromine is readily formed by oxidation of HBr and is an effective solvent for many minerals, especially sulfides. Liquid bromine dissolved in an organic solvent (methanol, ethanol, or carbon tetrachloride)[353] is generally used. Bromine selectively dissolves metallic iron from a mixture of oxides;[354-357] a bromine solution in ethyl ether is an efficient extractant for gold from large samples.[358]

3. Decomposition by HI

Hydroiodic acid has been used chiefly as a strong reductant in decomposition techniques. Its effect is further increased by addition of hypophosphorous acid or hypophosphite. Barium sulfate is reduced to the sulfide[359,360] by these reagents in the presence of HCl or H_3PO_4, and the H_2S liberated is absorbed in a solution of a Cd salt. This procedure has also been successful in the determination of sulfates in soils.[361] The decomposition of baryte is often incomplete; strontium sulfate is reduced more easily.[35] The decomposition of baryte in solutions containing H_2SiF_6, HI, and oxalic acid is complicated;[362] the reaction proceeds through barium fluorosilicate and oxalate. A mixture of HI and HCl releases H_2S quantitatively from galenite and sphalerite.[363] The decomposition of pyrite, chalcopyrite, and other sulfides can be hastened by adding a drop of mercury. An increase in the HI reactivity in this system is probably caused by electrochemical processes.[364]

4. Decomposition by HNO_3

Nitric acid is a strong acid, used most frequently for oxidative dissolution of minerals containing polyvalent elements, especially sulfides, selenides, tellurides, arsenides, and sulfoarsenides. Anionic and cationic components of the mineral are usually oxidized during the decomposition. The reaction products of HNO_3 itself (mostly NO) are gases, which are easily expelled by boiling the solution. Natural and synthetic phosphates, arsenates, and tungstates (e.g., scheelite and wolframite) are rapidly decomposed by this acid.

Resistant oxide minerals are not decomposed by HNO_3; rather, the acid is used (in combination with other acids) for their isolation from complex mixtures (e.g., with cassiterite, corundum, and nibium oxide minerals).[249] Mixed uranium oxides (uraninite) are readily dissolved in HNO_3 and the U(IV) present is oxidized to uranyl ions. Iron oxide ores are decomposed by HNO_3, but form insoluble products (called basic nitrates) when the solutions evaporate. The acid is equally unsuitable for dissolution of oxidic antimony ores.

Nitric acid has been used in analyses when other acids interfere in the final determination (e.g., in the determination of chlorides in apatite); however, very dilute HNO_3 (1+19) must be employed in order to avoid oxidation of the chloride.

The widest use of HNO_3 is in sulfide decomposition; a mixture of elemental sulfur and sulfates is usually formed. In order for oxidation to lead to a defined valence state (preferably sulfate), the dissolution must be carried out under rigorously maintained conditions and in the presence of other reagents, such as chlorate and bromine. The decomposition is unsuitable for the determination of lead in rich ores, as the sulfate formed reacts with Pb^{2+} to give $PbSO_4$, which separates along with the insoluble residue. Cinnabar is not dissolved even in concentrated HNO_3; only the fuming acid dissolves this mineral readily. Insoluble substances, called metaacids, are formed by reaction of Sb or Sn with HNO_3. However, this reaction is not suitable for separation of the two metals from other components, as the metaacids do not separate completely and other cations are adsorbed on their active surface. The formation of these compounds can be prevented by addition of organic oxyacids, especially tartaric and citric, and by carrying out the reaction at 20°C or at a slightly elevated temperature.[365-368]

The effect of HNO_3 is increased by the addition of other reagents (e.g., H_2O_2 or KI) which also accelerate the process; these procedures have been used[369,370] in the determination of Ge and Se in sulfides. A mixture of HNO_3 and Br_2 is an excellent solvent for sulfides and arsenides. Chlorate affects the decomposition process analogously. This decomposition type was successful in the determination of Re in molybdenite concentrates.[114] Because HNO_3 is an excellent reagent for sulfides, it has become the most widely used solvent for the determination of Ag in galenite and sphalerite[371] and in geochemical prospection. If the decomposition is carried out in the presence of $Hg(NO_3)_2$, AgCl is not formed from chlorides present as impurities in the decomposition mixture.[344,366] AgCl is readily adsorbed on the undecomposed fraction and the vessel walls.[372]

A mixture of HNO_3 and $HClO_4$ is employed for the oxidation of organic components in sedimentary rocks. By increasing the temperature during evaporation of $HClO_4$, the HNO_3 is easily removed. This process is more complicated with H_2SO_4, as nitrosylsulfuric acid is formed. Only repeated evaporation after solution dilution causes complete displacement of HNO_3.

The use of HNO_3 combined with mannitol is rather unusual, but in this way H_3BO_3 volatilization during evaporation[373] is suppressed. A similar effect is exhibited by addition of aluminum salts; this finding has been utilized in the determination of boron in aluminum alloys.[374]

5. Decomposition by Aqua Regia

Mixtures of HNO_3 and HCl are very powerful oxidants. Active chlorine is liberated by reaction between the two components, and nitrosylchloride is formed, which dissociates to give chlorine. A mixture containing 3 volume parts of concentrated HCl and 1 volume part of concentrated HNO_3 is called aqua regia; the reverse ratio of the two mentioned acids produces the Lefort (Lunge) mixture. As aqua regia readily dissolves metallic gold and its alloys, it has been successfully employed for the extraction of gold ores. This technique has gained importance, particularly in combination with AAS, where the procedure (even in a simple prospection modification) enables determination of Au at levels of parts per billion. Compared with the classical reduction fusion, the dissolution in aqua regia is much simpler and the results of the two procedures are in good agreement. Samples of 5 to 500 g are treated by this technique.[375] The sample is first ignited at 550 to 600°C to volatilize the sulfidic sulfur and oxidize the organic matter.[376,377] If the sample contains arsenopyrite, the ignition temperature is decreased to 480°C in the first stage; otherwise, volatile compounds are formed[378] by a reaction between Au and As and losses in Au occur. It is advantageous to add NH_4NO_3 for ignition, as the sample consistency is improved and the oxidation processes are hastened. If sulfides are not removed from the sample beforehand, elemental sulfur separates during treatment with aqua regia and gold is coprecipitated. Organic matter has similar effects. The completeness of the gold extraction from the sample depends on the amount of gold and the composition of the analyzed material. The losses are usually lower than 15%, with quartz losses often below 1%. Concentrations of Au were determined in the fraction undecomposed by aqua regia, both by reduction fusion and by activation analysis.[376-379] The radioisotope techniques indicated that the loss in Au is caused not only by the presence of undecomposable Au minerals, but also by adsorption of Au on the vessel walls and losses in the filter during filtration of the undecomposed fraction.[380] The extraction process is sometimes repeated[377] and the fraction of the gold liberated is further increased by the destruction of silicates[376,381] by HF. However, this was not observed with quartzes.[382,383] The content of Pd and Pt can be determined[384,385] at the same time as Au and Ag, but sperylite[386] and the natural platinum disulfide are not decomposed by aqua regia. The extraction procedure yields unsatisfactory results with chromites, in which part of Pd can be bound in the mineral lattice. The extraction recoveries for the platinum metals are probably subject to a systematic negative error.[387]

Aqua regia readily dissolves sulfides (including cinnabar), arsenides, selenides, and tellurides. Selenium and tellurium are oxidized to nonvolatile selenate and tellurate;[388] the oxidation process was controlled by radioisotopes.[304] Aqua regia further dissolves natural oxides of antimony. Antimony and arsenic are oxidized to nonvolatile pentavalency during the dissolution. The same decomposition technique was used for the determination of Hg in sulfides and sediments.[389,390] If the solution formed is evaporated in a water bath, there are no losses in Hg. Molybdenite is readily dissolved in aqua regia, the losses in Re being lower than 8%.[306]

Natural uranium oxides (uraninite) are easily decomposed in aqua regia. Industrially important tungsten minerals (wolframite and scheelite) are also dissolved.[391] Among sulfates, coelestine is attacked by aqua regia to ca. 25%, while baryte is virtually not attacked.

The Lefort mixture has been used most widely in the determination of sulfur in sulfides, especially in pyrite concentrates. The oxidation takes place at 20°C or even in cooled solutions; complete conversion of sulfides to sulfates is ensured by addition of chlorate or bromine.

C. Decompositions by Less Volatile Inorganic Acids

1. Decomposition by $HClO_4$

In decompositions of inorganic materials by $HClO_4$, specific properties of this acid as an oxygen donor and a dehydration agent are employed. All perchlorates, except those of K, Rb, and Cs, are readily soluble in water. $HClO_4$ has oxidizing properties only in hot concentrated solutions; when diluted, its oxidizing properties are lost.[392-395] Ferrous compounds are not oxidized in a 50% solution of the acid even at 100°C; in 70% acid, the oxidation is very rapid at 150°C. Hot concentrated $HClO_4$ reacts explosively with organic substances, but Teflon is resistant to its effects even at the boiling point of the azeotropic mixture (72.5%, 203°C). Inorganic substances containing organic impurities or components with reducing properties are thus decomposed by a mixture of $HClO_4$ and HNO_3. HNO_3 is partially dehydrated by $HClO_4$ and its oxidizing effect strongly increases at temperatures near 120°C. Organic substances are oxidized, but further increasing of the temperature leads to displacement of HNO_3 from the solution. H_2SO_4 causes $HClO_4$ dehydration, and an acid with a concentration higher than 85% is formed. This mixture oxidizes many substances even at a low temperature; for example, chromium(III) salts are oxidized at 138°C. H_3PO_4 has a similar effect. Gaseous chlorine and a small amount of H_2O_2 are the products of the $HClO_4$ decomposition, the latter causing back-reduction of the oxidation products. Its formation can be prevented by rapid cooling of the reaction mixture. Safety precautions must be observed in work with $HClO_4$; special apparatus, including fume cupboards, have been constructed for[396-398] series sample decompositions with $HClO_4$.

Perchloric acid is specifically used as a dehydration agent in the separation of silicic acid (limestones, dolomites, magnesites, cement, etc.). When mixed with H_3BO_3, it causes rapid decomposition of fluorite;[399-401] while quartz remains unattacked. However, this process of silicic acid precipitation has not been successful in silicate analysis; the results have also been considerably scattered with spinels.

The decomposition of monazite in $HClO_4$ solutions is very rapid[402-404] and the reaction mixture is turned orange by the Ce(IV) compounds formed. Apatite is also readily dissolved.[405] Extraction of phosphates from soils using $HClO_4$ is usually slow and often incomplete;[406] this may be caused by inclusions of phosphates in crystalline Al and Fe oxides, which are decomposed with difficulty.

Perchloric acid alone or in mixture with H_2SO_4 or H_3PO_4 oxidizes resistant minerals such as chromspinelides (including the industrially important mineral chromite).[407-411] The dissolution takes several hours even when the sample is very finely powdered. However, this decomposition is no longer used in the determination of the major component (chromium) as losses have been encountered, probably due to the formation of volatile CrO_2Cl_2; small amounts of chlorides are always present in the reaction mixture as a product of $HClO_4$ decomposition.

$HClO_4$ is frequently used for decompositions of rocks in combination with HF (see Section IIIA). In geochemical prospection for molybdenum, a $HClO_4$ and HNO_3 mixture did not yield good results and Mo compounds were not completely extracted from the analyzed soils;[412] this mixture, however, very rapidly dissolves practically all sulfidic minerals.[351] Lead(II) perchlorate (formed during the decomposition of galenite) is thermally unstable and decomposes at temperatures above 130°C, yielding sparingly soluble compounds.[413,414] These products are most rapidly dissolved in alkaline tartrate or citrate; this method of dissolving the precipitate has been employed in the determination of Ag and Bi in lead ores.[414,415]

Data on the behavior of selenium are contradictory. Although volatilization of Se compounds has been proven,[296,416] $HClO_4$ combined with HNO_3 and H_2SO_4 has been used for decompositions of sulfidic compounds.[417-419] During prolonged evaporation, selenium is oxidized to selenate. Tellurium compounds do not volatilize under identical conditions.[304,420] Losses in mercury occur[421] only after an increase in the reaction mixture temperature above 200°C. Volatile Re_2O_7 can be separated from molybdenite concentrates[422] by distillation from a $HClO_4$ and H_2SO_4 solution. RuO_4 and OsO_4 distill when boiled with $HClO_4$; this decomposition procedure has been employed for isolation of these compounds from native Ag,[423] Pt-rich chromites,[424] stone meteorites,[425] and dressing products of Pt ores.[426] Losses in iridium also occur under the same conditions.[427]

Perchloric acid has an important application in the so-called wet combustion of coal. Its combination with periodic acid is especially effective,[428] as periodic acid attacks the bonds in organic compounds and converts these compounds into smaller molecules readily oxidizable by $HClO_4$. The oxidation course is complicated. During the oxidation of organic matter, periodic acid is reduced to iodic acid and finally to iodine (I) perchlorate.

2. *Decomposition by H_2SO_4*

Hot concentrated H_2SO_4, often employed for decompositions of inorganic substances, acts as a mild oxidant. Its effect is much weaker than that of $HClO_4$. Stannous compounds are oxidized to stannic (e.g., in dissolution of sulfides) and ferrous to ferric. The acid is reduced to H_2S (especially in the dissolution of some alloys), elemental sulfur, or SO_2. Sulfur dioxide is commonly formed during decompositions of mineral materials and can be readily expelled by boiling the diluted reaction mixture. The dehydrating properties of H_2SO_4 are most pronounced and are analytically utilized in the precipitation of silicic acid. Simultaneously, the alkaline earth and lead sulfates are precipitated, as are the anhydrous sulfates of transition metals, which are difficult to rehydrate and dissolve (especially nickel, cobalt, and ferric sulfates). The insoluble sulfates adsorb many cations. Although hot concentrated H_2SO_4 acts as an oxidant, it is combined with other acids and oxidants (e.g., HNO_3, $HClO_4$, H_2O_2, MnO_2, and $KMnO_4$) to accelerate the decomposition. The oxidizing effect of these substances is further increased by the dehydrating effect of H_2SO_4 under suitably selected conditions.

Sulfuric acid is rarely employed for dissolution of oxides, as the reaction is slow and mostly incomplete. Corundum and cassiterite are not decomposed, and rutil is only partially decomposed, even if the reaction mixture temperature is increased by addition of an alkali sulfate. Anatase, however, is dissolved. The degree of decomposition of pitchblende increases with increasing UO_2 content; oxide uranium ores are rapidly and quantitatively decomposed by a mixture of H_2SO_4, HNO_3, and HF. Composite oxides of the spinel type are not decomposed by H_2SO_4. Certain titanates, especially loparite, ilmenite, titanomagnetite, titanite, and perovskite, are better dissolved. Depending on the reaction conditions, $TiOSO_4$ or $Ti(SO_4)_2$ may be formed.[429]

Among phosphates, monazite[430,431] dissolves in H_2SO_4; dissolution in H_2SO_4 was also employed technologically for obtaining Th, U, and the rare earths from monazite concentrates. Amblygonite, tourquoise, and other phosphates[432] are also decomposed. Wolframite and scheelite are dissolved in H_2SO_4, but this decomposition procedure is not very advantageous because of the strong adsorbing properties of the tungstic acid precipitated. Some silicates of the zeolite group are smoothly dissolved in H_2SO_4 and silicic acid precipitates. This procedure can be employed analytically in the determination of the major components of biotite: the finely powdered mineral is decomposed after it is boiled for 30 min in H_2SO_4 or in a mixture of H_2SO_4 and HCl. Fluorite is readily decomposed when evaporated with H_2SO_4; insoluble calcium sulfate precipitates and is dissolved by heating with HCl.

Sulfuric acid is most frequently employed for the decomposition of arsenides and sulfidic arsenic and antimony ores.[433] However, oxidic antimony ores (valentinite, senarmontite, etc.) are quite resistant to the effect of H_2SO_4; the insoluble residue is further dissolved in tartaric acid or aqua regia or is decomposed by fusion. Sb(V) oxides are reduced during the decomposition. The reaction is generally complicated by the presence of the sulfide component of the ore, which is oxidized by H_2SO_4 to elemental sulfur; this mixture has reducing properties. No reduction of pure Sb_2O_5 has been observed[434] when it is evaporated with H_2SO_4. Decomposition with H_2SO_4 and S is utilized analytically in solution preparation for the determination of As in ores.[435,436] Cinnabar is dissolved by heating in a mixture of H_2SO_4 and $KMnO_4$. If the material analyzed contains organic matter, nitric acid is added to the mixture. The procedures developed have been applied to the determination of Hg in sulfidic ores,[437-439] rocks,[440,441] separated heavy minerals,[442] and coal.[443,444] Gold inclusions in rocks are not dissolved in H_2SO_4, but tellurides and selenides of gold are decomposed. The SO_2 dissolved in H_2SO_4 reduces Au^+ from the minerals decomposed, and the gold is adsorbed on the undecomposed fraction. This procedure is employed for preliminary separation of Au from other components.

During solution evaporation to SO_3 fumes, most of the Se volatilizes, but the loss is decreased considerably by adding HNO_3.[297,445] However, tellurium compounds do not volatilize.[304] Even graphite is oxidized in a 9 + 1 mixture of H_2SO_4 and the Caro acid at 150°C.[446]

3. Decomposition by H_3PO_4

Phosphoric acid is especially suitable for dissolution of oxide compounds. Its very low volatility and pronounced complexing properties are utilized. Phosphoric acid readily displaces volatile inorganic acids from their salts and reinforces the oxidizing properties of sulfuric acid due to its strong dehydrating effect. Condensation reactions take place when H_3PO_4 is heated with forming polyphosphoric acids which substantially accelerate the dissolution of the analyzed material because of their complexing properties. Phosphate complexes of some transition metals are stable even in strongly acidic media. Although H_3PO_4 has no oxidizing properties, even at temperatures near 300°C, it strongly affects redox equilibria by formation of variously stable complexes with the individual members of redox couples (e.g., Fe(III)/Fe(II), U(VI)/U(IV). Concentrated H_3PO_4 (density = 1.92) is much more effective than the dilute acid. The oxidation of Fe^{2+} by atmospheric oxygen is very rapid in these concentrated solutions, while U(IV) compounds are stable in concentrated H_3PO_4. Considerable disadvantages of these decomposition techniques are that analytical procedures (especially methods of group separation and spectrophotometric methods) are complicated by the presence of excess H_3PO_4 and phosphates insoluble even in dilute acids are formed with many elements (e.g., Ti, Zr, Th, U(IV), Bi, rare earths).

A mixture of H_3PO_4 and H_2SO_4 or $HClO_4$ is an excellent solvent for oxide iron ores.[447] The decomposition is complete 5 to 10 min after H_2O is expelled from the reaction mixture by boiling. Fused Al_2O_3 can be decomposed by the same mixture.[448] Composite polyvalent uranium oxides (U_3O_8) are also dissolved in H_3PO_4; the stability of U(IV) compounds in this medium has been utilized in the determination of U(IV).[449,450] The decompositions are usually carried out in Pt, quartz, glass, or Teflon vessels.

Oxidic Mn ores are readily dissolved in solutions containing H_3PO_4 and H_2O_2; at higher temperatures, Mn^{2+} ions are oxidized by atmospheric oxygen in anhydrous H_3PO_4 to purple complex compounds of tervalent manganese. The oxidation can be accelerated by the addition of $HClO_4$. The proposed dissolution processes have been successful in the determination of FeO and active oxygen in Mn ores and other minerals.[451-456] If higher Mn oxides are present in the analyzed substance, they are selectively reduced by oxalic acid, and FeO is determined by oxidimetric titration.[456,457]

Phosphoric acid has found widest use in decompositions of chromites. The decomposition efficiency is increased by the formation of phosphate complexes with the major mineral components. The solutions obtained were used for the determination of principal elements in minerals[458] by AAS.[459] The conditions for the determination of FeO in chromite and Cr ores are much more demanding. The decomposition is carried out under a perfectly inert atmosphere or in the presence of a defined excess of an oxidant at temperatures varying from 270 to 360°C. Both procedures have certain drawbacks. FeO is oxidized very easily in solutions of H_3PO_4 and H_2SO_4 at the given temperatures and the oxidants added are not very stable under these conditions. SO_2 is liberated in the reaction mixture by the reducing effect of FeO and is absorbed[460] in $K_2Cr_2O_7$. If the decomposition takes place in a CO_2 stream, the CO_2 is reduced to CO and the latter is oxidized in the absorption vessel containing dichromate.[407] Dissolution of chromite in a mixture of H_3PO_4 and H_2SO_4 with excess oxidant must be performed rapidly; otherwise, the ceric salt[461-464] or vanadic acid[220,465,466] added is spontaneously reduced. On the basis of critical evaluation of these procedures, the decomposition in the presence of excess ceric salt is preferred,[461] as vanadic acid is less stable and is 16 to 20% reduced. Manganese(III) compounds have also been successfully applied;[467,468] they are prepared by Mn^{2+} oxidation with permanganate in a H_3PO_4 medium.

Natural carbonates readily release carbon dioxide when treated with H_3PO_4; the reaction is slowest with siderite and magnesite,[469] for which 85% H_3PO_4 must be employed. The CO_2 liberated is at present mostly determined gas chromatographically[470,471] or by coulometric titration.[469] The procedure can also be applied to sedimentary rocks with a high content of organic substances; they are not substantially attacked even by hot concentrated H_3PO_4, but the organic substances are oxidized when CrO_3 is added. A mixture of H_3PO_4 and CrO_3 (the so-called Dixon mixture)[472] has found wide application, especially in the determination of organic carbon in rocks and soils.[473,474]

Even resistant silicates (e.g., tourmaline, biotite, and garnet) are dissolved in H_3PO_4 with H_2SO_4 (2 + 1) added. Quartz remains unattacked,[475] so this dissolution procedure can be used for the determination of quartz in the presence of silicates. If a silicate contains FeO, an equivalent amount of SO_2 is formed (by reduction of H_2SO_4) which is determined by automated iodometric titration.[476] FeO can be determined in tourmalines after mineral dissolution in H_3PO_4 containing NH_4F and KHF_2. The optimum decomposition temperature[477] is 210 to 220°C; at higher temperatures, uncontrollable oxidation of FeO occurs. The combination of H_3PO_4 and HNO_3 makes an excellent solvent for ashes; the silicate lattice is destroyed and the Ge present is released[478,479] without adding HF. Sulfides[480] are decomposed equally smoothly; a mixture of $HClO_4$ and H_3PO_4 is generally used in order to accelerate the dissolution process.

A $SnCl_2$ solution in H_3PO_4 is a strong reductant and readily liberates H_2S from pyrite and other sulfides.[481-485] A mixture containing H_3PO_4, red phosphorus, NaI, and propionic acid[486] exhibits similar effects. The extent of decomposition for the determination of small amounts of S was verified by analyzing standard rocks. The H_3PO_4 condensation products combined with $SnCl_2$ reduce natural sulfates to H_2S. Selenium compounds are reduced to H_2Se. This condensation product decomposes glasses and other natural silicates[487] at an elevated temperature.

D. Decompositions by Ion Exchangers

Ion exchangers are solid acids or bases and, therefore, can be employed as solvents for solid phases. This decomposition technique has not been used very widely, even though some advantages are evident. No impurities or large amounts of salts are introduced into the solution analyzed; moreover, cations are separated from anions during the decomposition.

The solubility of a solid in water at a given temperature is expressed by the solubility product. If some kind of ion is removed from a saturated solution of a sparingly soluble substance by ion exchange, the equilibrium between the solid phase and the solution is disturbed and the solid begins to dissolve. The decomposing effect of an ion exchanger depends on the ion distribution coefficient between the ion exchanger and the solution. Optimum conditions are created when the hydrogen ions liberated from the strongly acidic cation exchanger in the H^+ cycle react with the anion of the compound being decomposed and are thus removed from the system. This occurs during decompositions of carbonates, sulfides, or phosphates. When an anion exchanger in the OH^- cycle is simultaneously employed, the decomposition will be hastened by simultaneous sorption of the anions and by the neutralization of the solution by the OH^- ions liberated. Very small amounts of ion exchangers are required and can be calculated from the values of the solubility product, the selectivity coefficient, and the dissociation constants of the acids formed.[880]

Phosphates and fluorophosphates can be decomposed using ion exchangers; alkaline earth carbonates; and natural sulfates of calcium, barium, lead, and iron. The complexing ion exchanger Dowex A1, with iminodiacetic functional groups,[881] has also been employed for the decomposition of calcium carbonate. Natural phosphorites are decomposed in aqueous suspension by a combination of cation and anion exchangers: the two ion exchanger kinds can then be separated mechanically on screens. The insoluble residue remaining after the decomposition did not contain a detectable amount of phosphate.[882] Decomposition of an aqueous suspension of the rock by a cation exchanger for the determination of fluoride has been described.[883]

In addition to decompositions of simple natural compounds, dissolution of melts by a strongly acidic cation exchanger has been described.[614,615] A rock is decomposed by fusion with an alkali metaborate, and the mechanically crushed melt is agitated with the exchanger. The sorbed cations are either eluted by an acid from the separated exchanger and determined by AAS in the eluate or the dried resin is directly analyzed spectrochemically. The purpose of the decomposition is rapid separation of cations from excess anions coming from the fusion agent and from silicic acid, as both of these components adversely affect the subsequent spectrochemical determinations.

IV. DECOMPOSITION BY FUSION

Fusion belongs among energetic decomposition procedures; it is employed with analyzed materials insoluble in acids and often also serves for partial separation in the analyzed mixture. During fusion, compounds soluble in water or in acids are formed from insoluble substances. An important factor in fusion is a high temperature causing rapid heterogeneous reactions between solids and the melt. A general drawback of fusion procedures is the necessity of using considerable excesses of fusion agents (more than the sample weight), leading (together with corrosion of the vessels used, crucibles, and dishes) to serious contamination of the solutions to be analyzed. Excess neutral salts complicate many analytical reactions.

Impurities introduced into the solution prevent the determination of minor and trace elements.

Fusion procedures can be classified according to the heterogeneous reactions taking place in the fusion agent substance system as follows:

1. Alkaline fusion – fusion with carbonates, hydroxides, peroxides, and borates
2. Acidic fusion – fusion with pyrosulfates, hydrofluorides, fluorobarates, and boric oxide
3. Oxidizing-reducing fusion – alkaline fusion agents mixed with oxidants or reductants are usually employed, including alkaline fusion in the presence of elemental sulfur.

A. Alkaline Fusion

Basic properties of the above alkaline fusion agents are discussed in this section. Fusion with borates has gained considerable importance in combination with atomic absorption spectrometry (see Section IV.C).

Sodium and potassium carbonates or their equimolar mixture are the alkaline fusion agents employed most frequently. The melting points are 850, 980, and ca. 500°C for the sodium, potassium, and sodium-potassium salts, respectively. Because commercial substances, especially sodium carbonate, contain rather high concentrations of silicon and calcium oxides, hydrogen carbonate is recommended as the fusion agent. This can readily be prepared very pure and converted into carbonate by heating at 300°C. Alkali carbonate melts partly dissociate forming the appropriate oxides, which seriously corrode the fusion crucible. This process is especially marked with lithium carbonate, which is quantitatively converted into the oxide at ca. 710°C. However, the carbonate decomposition is suppressed to a minimum by fusing under a carbon dioxide atmosphere. Cesium carbonate has been employed in special silicate decompositions. After precipitation of silicic acid, the solution is used for the flame photometric determination of alkali metals.[488]

Platinum or platinum alloy crucible is most frequently used for carbonate fusion. Alloying with iridium or rhodium improves the mechanical strength of platinum, while the addition of gold (5%) or zirconium (0.1%) increases its chemical resistivity. Platinum is corroded not only by sodium oxide produced by the thermal dissociation of sodium carbonate during fusion but chiefly by reaction with ferrous compounds present in the melt. The platinum-iron alloy formed during fusion causes a loss of iron in the material analyzed. It could be removed either by repeated extraction with hot concentrated hydrochloric acid or by fusion with pyrosulfate. In decompositions of iron(II)-rich silicates, the amount of platinum in the melt may amount to 10 mg. Corrosion of platinum crucibles and platinum distribution during the classical silicate analysis was studied.[489]

Certain metals volatilize during carbonate fusion: arsenic and selenium partially and thallium and mercury completely.[490] The behavior of a number of cations was studied during melt extraction with water. Most carbonates may form colloidal solutions during the extraction of the melt with water and thus may pass into the extract.[491]

Sodium carbonate is one of the oldest fusion agents. Most inorganic substances can be decomposed by it, but its widest application is in silicate analysis. An alkaline mono- or disilicate is formed in the reaction with silicon dioxide and can readily be dissolved in mineral acids. Aluminum from alumosilicates is partially converted into aluminate and partially forms basic and composite carbonates with other cations. Most silicate minerals can be decomposed by this fusion agent; completeness of the decomposition depends on the grain size of the material to be decomposed, the duration of the fusion, and the temperature used. Silicates rich in aluminum, as well as beryl, zircon, and titanite are decomposed poorly.

Carbonate fusion is oxidative, especially when the air is in contact with the melt, or the fusion is performed in an oxygen atmosphere. The oxidizing effect can be increased by adding additional reagents, such as nitrates and chlorates; however, corrosion of the platinum vessels increases proportionate to the concentration of oxidating agents. The procedure can be made more universal by adding sodium tetraborate, an alkali hydroxide, peroxide, metal oxides, etc. These mixtures are then efficient fusion agents for many resistant minerals. In analytical practice, aqueous extracts of carbonate melts are frequently employed; they have been used in the separation of anionic components or in the isolation of sparingly soluble carbonates and hydroxides. Classical carbonate fusion will long remain the basic decomposition technique for inorganic materials. Its complete replacement by acid decompositions at elevated temperatures depends on whether sufficiently resistant inlays for pressure vessels will be discovered, permitting the use of temperatures near 500°C.

Alkali hydroxides are other efficient alkaline fusion agents, permitting decomposition of most oxygen-containing and silicate minerals. The melting points of these substances (NaOH, 328°C; KOH, 360°C) are somewhat lowered by the presence of water and carbonates. They are quite volatile when fused; the cooled melt is strongly hygroscopic. As hydroxides release water during fusion and melt splashing occurs, the fusion agent is usually first dehydrated at the melting point and the sample is then placed on the solidified melt.[249,492] Dehydration of fused hydroxides is not complete[493] and the equilibrium, $2OH^- = H_2O + O^{2-}$, is established.

Fused hydroxides seriously corrode the fusion vessel material. Zirconium is most resistant to their effect, along with gold,[494] silver, and nickel. Teflon is not corroded by a fused mixture of sodium and potassium hydroxides at 280°C. For some decompositions, iron, corundum, and similar crucibles can also be used. Platinum is dissolved by fused hydroxides only in the presence of atmospheric oxygen. The extent of corrosion was studied experimentally;[495] it has been found that the metal is decomposed relatively far under the surface. Following repeated leaching of the crucible which contained $6\,M$ HCl, 6×10^{-5} g of the metal was still found in the fifth extract. When the fusion is carried out in a platinum crucible under a rigorously inert atmosphere, its losses are somewhat lower than in fusion with sodium carbonate.[496]

For the decomposition of most mineral materials, approximately a tenfold excess (over the sample) of the fusion agent is sufficient. The decomposition generally takes about 5 to 15 min; some resistant minerals must be decomposed longer. Aqueous or alcoholic solutions of hydroxides can also be used for the decomposition. After sufficient dampening of the material, the mixture is evaporated to dryness. Heating of the upper part of the crucible must be prevented during fusion or undesirable creeping of the melt up the walls occurs. The cooled melt is easily leached with hot water and falls apart very rapidly. Melt leaching with hydrochloric acid vapors in an evacuated space has also been described.[497]

Losses in some elements (e.g., Hg, Se, Tl, and Re) occur during the fusion. There are considerable losses in tellurium when the fusion is performed in iron or nickel crucibles; when using sintered corundum crucibles there is no loss.[304]

Fusion with alkali hydroxides in silver crucibles is an ideal decomposition technique for the determination of iron in silicate analysis. Iron is not reduced in this medium and does not form alloys with silver. Fusion decomposition with hydroxides in a platinum vessel under a pure nitrogen atmosphere[490] is an effective technique for the determination of trace elements. Among mixed fusion agents, mixtures with alkali peroxides and especially alkali cyanides are effective fusion agents for cassiterite. Hydroxide fusion is advantageously employed as a procedure for the separation of acidic and amphoteric elements of the V and VI groups from ions forming sparingly soluble hydroxides.

Sodium peroxide is undoubtedly the most effective alkaline fusion agent. In addition to having an energetic decomposing effect, the fused peroxide is also a strong oxidant. Most cations are oxidized to their highest valencies during fusion. Two crystalline modifications of this compound are known;[498] the behavior of the substance has often been studied using thermogravimetric analysis.[499] It has been found that composite sodium and hydrogen peroxides are formed when dried *in vacuo*. Similar compounds are also formed on drying in the air. The peroxide melts at 495°C without danger of explosion. The vapor pressure above its melt is relatively high; at a higher temperature, the substance decomposes to sodium oxide and oxygen. The danger of explosion increases if easily oxidizable substances (e.g., organic compounds, graphite, sulfides, or powdered metals) are present in the mixture being decomposed. Although the peroxide decomposes practically all minerals, its use in chemical analysis is limited to certain determinations; it is rather rare in complete analyses because the commercial substance is usually insufficiently pure and the analyzed sample is seriously contaminated by the crucible material during fusion. Metallic zirconium, gold, and silver (in that order) resist fused peroxides. However, nickel, iron, or sintered corundum crucibles frequently suffice. Platinum can be protected against the peroxide effect by a layer of sodium carbonate melt formed prior to the decomposition. Analogously, nickel crucibles are protected by a solidified melt of an alkali hydroxide. The loss in zirconium crucible material is about 5 mg/gram of the fusion agent during normal fusion time (5 to 10 min); this is not a small amount, but is negligible compared with the loss of silver or nickel (100 to 200 mg). Older, recrystallized zirconium is lost to a much greater degree than the new material. A comparative study was conducted[500,501] on the corrosion of various fusion crucible materials during peroxide fusion.

In addition to the classical fusion procedure, an explosive decomposition is also employed; the sample is mixed with peroxide and carbon, and the mixture is ignited. The decomposition reaction temperature is high (1450°C), but the crucible is not damaged.[502] Explosive decompositions can also be carried out in closed pressure vessels, such as the Parr autoclave, etc. Other substances supporting the reduction must also be present in addition to the peroxide.

Mixtures of sodium peroxide and carbonate, hydroxide, or metal oxides are also frequently used for decompositions. Most of these additives retard rapid or even explosive decomposition reactions in the decomposition of sulfides, etc. Barium peroxide, which has similar decomposing effects, is employed less frequently.

The peroxide fusion decomposition is advantageous for those elements which form readily soluble anions of the acid of the highest valence state in alkaline media. By leaching the melt with water, amphoteric elements can be readily separated from weakly basic elements. The peroxide is also an outstanding fusion agent for very resistant minerals, especially composite oxides of the spinel type (viz., chromites, cassiterite, oxygen-containing and silicate compounds of zirconium, niobium, tantalum, and platinum metal minerals, etc.).[408,411,503-505] Peroxide has been used in rapid analyses of silicates when the analyzed material must be quantitatively dissolved.[506]

B. Acidic Fusion

1. Decomposition by Fusion with Hydrogen Sulfate and Disulfate

This is a weakly oxidizing acidic fusion, employed chiefly for decompositions of oxygen-containing compounds. A number of sulfides and phosphates can also be decomposed using this procedure, but it has been used only rarely for these purposes. Alkali metal hydrosulfates dissociate water in the initial stage of heating and are converted into pyrosulfates. As this reaction is rapid and the melt fumes and splashes, it is more advantageous to fuse directly with pyrosulfate or to dehydrate hydrosulfate before sample introduction. Sulfur trioxide, dissociated from pyrosulfate at a higher temperature, is the active component of the fusion mixture. Pyrosulfate is converted into inactive alkali sulfate. Therefore, it is necessary to add a little sulfuric acid to the solidified and cold melt (especially after prolonged fusion) in order to form new hydrosulfate, so that the fusion can be carried out for the required time. The sodium salts are, in many respects, more suitable than the potassium salts, as they form more soluble binary sulfates with aluminium, zirconium, and other metals. However, their melting point is somewhat lower than that of the potassium salts which may cause incomplete decomposition. The lower thermal stability of sodium pyrosulfate is also disadvantageous. It is difficult to prepare anhydrous sodium pyrosulfate. Dehydration in the air leads to a substance with about 70% content of the active component, since pyrosulfate begins to decompose in the melt before all the water has escaped. A product suitable for analysis is obtained by heating the hydrosulfate for 24 hr at 170°C *in vacuo.* The water liberated by the reaction is freezed out of the system.[507]

Considerable excesses of the fusion agent must be used in fusion of most materials. However, too much neutral salt is introduced into the analyzed solution which may unfavorably affect further analysis. Commercial substances are not always sufficiently pure and contain various cations which prevent the determination of traces of elements. These disadvantages of alkaline fusion agents can be eliminated by using ammonium pyrosulfate. The reagent itself is somewhat less effective than the potassium salt, but can be readily decomposed and removed after completion of the decomposition by evaporation at an increased temperature. The fusion can be carried out under a tightly closed lid at temperatures as high as 475°C. At higher temperatures, the melt boils quietly, without forming froth. Ammonium pyrosulfate is supplied pure enough for analysis.[508] Ammonium hydrosulfate was used for decompositions of sulfides of Fe, Cu, Pb, and Zn.[509] Cesium pyrosulfate is a special fusion agent, used because of the subsequent flame photometric determination of the alkali metals; cesium ions regulate the ionization processes in the flame. Persulfate is used only rarely as a fusion agent for some rare earth oxides and phosphates. Pyrosulfate fusion is frequently combined with preliminary acid decomposition. Silicate crystal lattices are destroyed by sulfuric and hydrofluoric acids, and the salts formed are decomposed by fusion with pyrosulfate. Combined fusion with an alkali fluoride and pyrosulfate is also effective; this decomposition technique is universal and is advantageous because the acidic character of the melt prevents the formation of insoluble bases and increases the effect of fluoride ions. Moreover, the fluoride, which interferes in the subsequent analysis, is quantitatively removed during the fusion. A number of oxygen- and sulfur-containing ores can be decomposed by fusion with a mixture of ammonium hydrosulfate and chloride or nitrate. The fusion takes place at low temperatures and can be carried out in a glass apparatus.[509]

For pyrosulfate fusion, fused quartz or predominantly quartz glasses, such as Vycor®, are the most suitable materials. Test tubes of borosilicate glass are suitable for routine analysis. Corrosion of this material is negligible during fusion, and the melt virtually does not form froth on contact with a nonmetallic material. Pyrosulfate does not damage gold and iridium at temperatures as high as 600°C and Teflon up to 280°C. On the other hand, fused pyrosulfate causes considerable corrosion of platinum ware; the loss in the metal is several milligrams in a single operation and increases with increasing fusion duration. Ammonium pyrosulfate is a less corrosive reagent for platinum than are the alkali metal salts, but the fusion is slower and must be performed in a quartz crucible. Sintered corundum is also not a very suitable material for pyrosulfate fusion crucibles, as colloidal aluminum oxide is formed during the fusion and passes into the melt extract.

Pyrosulfates belong among the few fusion agents that reliably decompose the natural aluminum oxides, corundum, sapphire and ruby, and their synthetic equivalents. Hydrated aluminum oxides (such as diaspor, gibbsite, and böhmite), which are major components of bauxites, are also readily decomposed, as are oxygen-containing iron ores. As the latter can readily be decomposed by mineral acids, pyrosulfates are used for subsequent fusion of insoluble residues in which aluminium, chromium, titanium, and other oxides are concentrated.

Alkali metal pyrosulfates are excellent fusion agents for all titanium dioxide modifications (rutil, anatas, and brookite). Iron-, tin-, niobium-, and tantalum-containing rutil varieties are readily decomposed. The melt extract in H_2SO_4 was employed for direct determination of titanium, iron, niobium, phosphorus, and zirconium.[510-512] Natural titanates, ilmenite, perovskite, and pyrofanite are decomposed well by pyrosulfates. Fusion was used for subsequent determination of iron and titanium,[513] chromium,[514,515] and vanadium.[516]

Pyrosulfates can be used for analysis of many binary oxides of di- and tervalent cations, called spinels. Chromium-containing compounds require a prolonged fusion time; the decomposition is complicated particularly by the presence of larger amounts of silicon dioxide (e.g., in chromium ores and fireproof chromite ceramics).[408] For these materials, a mixed fusion agent (sodium fluoride and hydrosulfate) is more suitable.[411] Pyrosulfate fusion has been used to determine titanium in chromium ores and chromites.[517]

Milner[518] studied the behavior of many ignited oxides during fusion with ammonium hydrosulfate. Uranium, vanadium, and zirconium oxides are decomposed completely after 3 hr of fusion at 400°C. Titanomagnetite isolated from kimberlites is decomposed after 45 min at 150°C; ammonium hydrosulfate is first dehydrated slowly. A mixture of the fusion agent and ammonium hydrofluoride is more suitable for silicate materials. This decomposition procedure was used to determine platinum metals.[250]

Pure tin dioxide (cassiterite) is only negligibly decomposed by fusion with a pyrosulfate. However, if the mineral contains larger amounts of niobium and tantalum, these elements can be dissolved during fusion. A mixture of sodium fluoride and pyrosulfate is an effective fusion agent for cassiterite.[519] Natural thorium oxides, bröggerite, and thorianite often containing uranium and rare earths are readily soluble in the pyrosulfate melt. The melt is advantageously dissolved in complex-forming electrolytes, such as tartaric and oxalic acids. Most oxygen-containing minerals of niobium and tantalum, especially columbite, tantalite, loparite, and others, are completely decomposed by fusion with pyrosulfates. A scheme has been developed for complete analysis of these compounds after the above decomposition procedure.[520] If tantalum predominates over niobium in the sample, a sodium salt is used as the fusion agent, since potassium ions lead to the formation of sparingly soluble binary rare earth sulfates or fluorotantalate. The melts must be extracted by complex-forming electrolytes. A photometric determination of niobium[521] and tantalum[522] in poor ores using this decomposition procedure was described.

Tungstates, such as scheelite and wolframite, can be readily decomposed by pyrosulfates. This decomposition procedure was employed in the gravimetric determination of tungsten in minerals[523] and in the photometric determination of small amounts and traces of tungsten in ores,[524] soils,[525] and rocks.[525,526] It is suitable for the determination of silicon dioxide in wolframite concentrates[527] and niobium in separated tungsten minerals.[528]

Although pyrosulfate fusion has a limited importance in silicate analysis, it is often employed in geochemical prospecting to study rocks, soils, stream sediments, and plants. The decomposition is effectively performed in glass test tubes, and the melt extract is used for direct photometric or AAS determination of the element. Organic substances are completely destroyed by the fusion. The determinations of zinc in ores,[529] traces of molybdenum in sediments[530] and soils,[531] vanadium,[532] and antimony[533] have been described. The fusion decomposition for geochemical purposes is equally effective as dissolution in mineral acids.[534] Tellurium volatilization during the fusion is negligible.[304]

In order to decompose silicates completely, it is best to first treat the sample with mineral acids (H_2SO_4 and HF) and to fuse the residue with pyrosulfate. The solution obtained is used for an AAS determination[535] of major rock components, for example for the determination of aluminum in an NBS standard feldspar[536] and tin in standard rocks.[537]

2. *Decomposition by Fusion with Acidic Fluorides and Fluoroborates*

Potassium hydrofluoride and ammonium fluoride are used for decompositions of oxides, niobates, tantalates, and silicates which are otherwise decomposed with difficulty. As certain elements volatilize as fluorides during fusion, this decomposition procedure cannot be used for complete analysis. A large proportion of silicon volatilizes; it can be quantitatively removed from the system and the melt solution can be used to determine the individual components.[167] The fusion is performed in platinum crucibles; to remove fluoride, the melt is heated with sulfuric acid or is further fused with the hydrosulfate formed. When using 2 g of potassium hydrofluoride, a loss of 0.15 mg of platinum was observed.[539] In addition to silicon, molybdenum, niobium, and tantalum also partly volatilize.[538]

The decomposition itself proceeds in two steps: first, the fusion agent, potassium hydrofluoride dissociates at a low temperature to yield free hydrofluoric acid, which effectively destroys the crystal lattices of the mineral phases present. This fusion stage must proceed at a low temperature and should last as long as possible. The end of the thermal decomposition is indicated by solidification of the melt. During the second phase of decomposition, the temperature is slowly increased up to 700 to 800°C and is maintained until a transparent melt is formed. Ammonium fluoride acts similarly: ammonia is dissociated at 145°C and free hydrogen fluoride is formed. An advantage of ammonium fluoride is that an excess can be readily destroyed. However, it is not as universal a reagent as potassium hydrofluoride, as it does not decompose minerals of the Al_2SiO_5 group (i.e., sillimanite and cyanite, as well as zircon, rutil, and others.[540] Decomposition effectiveness is increased by the formation of stable fluoride complexes (of berylium, niobium, tantalum, zirconium, etc.) in the melt. The fusion is also advantageous for decompositions of rare earth minerals, as these are removed from the analyzed mixture as sparingly soluble fluorides formed during the decomposition. Potassium hydrofluoride is one of the few agents that reliably decompose the silicates beryl and zircon. The natural zirconium oxides cyrtolite and baddeleyite[541] are readily decomposed during fusion, as are the niobotantalates columbite and tantalite[542,543] and a mixture of complex oxides of the so-called heavy minerals.[442] The potassium hydrofluoride fusion is suitable for the decomposition of rare earth phosphates, monazite, and xenotime. Most procedures utilize the insolubility of the rare earth fluorides formed during the decomposition for their isolation, followed by the determination of individual elements, especially uranium and thorium.[544-546] Rutil is rapidly decomposed during fusion with potassium hydrofluoride; 50 mg of the mineral is dissolved in a tenfold excess of the fusion agent within 30 min.[12] The use of sodium fluoride as a suitable fusion agent for the decomposition of beryl[547] and for the spectrochemical determination of beryllium in some of its minerals has been described.[548] Fusion with ammonium hydrofluoride was employed for isolation of the platinum metals and oxygen-containing minerals from kimberlites. The rock (50 g) is decomposed in a nickel dish containing 500 g of the fusion agent at a controlled temperature of 150 to 170°C, the fusion is terminated at 600°C and is repeated after the addition of hydrofluoric acid. Isolated oxygen-containing minerals, especially titanomagnetite, are decomposed by fusion with hydrosulfates.[250] An analogous procedure has also been described for isolation of ruthenium and osmium from enriched ores, with subsequent neutron activation.[549]

Fluoride fusion is frequently used to determine certain components of silicate rocks, soils, glass-making sand, and ceramic products. It has been used to isolate radionuclides,[550,551] alkali metals,[552] rare earth metals,[553] and thorium.[554] This decomposition procedure is often combined with subsequent fusion of the undecomposed phases with hydrosulphates; it has been used in the determination of traces of tin in rocks[555] and of niobium and tantalum in ores,[556] and in other procedures.

Sodium and lithium fluoroborates have proven useful as fusion agents for especially resistant silicates. Sodium fluoroborate melts at 400 to 450°C; its decomposition occurs at a substantially higher temperature. Metafluoroborates have a similar effect. This fusion agent is prepared by mixing and fusing equivalent amounts of sodium fluoride and boric acid at 750 to 1000°C, forming a transparent melt. The composition of the products roughly corresponds to the formula $Na_2B_2O_3F_2$. This fusion was introduced into analytical chemistry by Rowledge,[557] who employed it for the determination of FeO in resistant minerals. Metafluoroborates effectively decompose silicates with high contents of aluminum (for example, cyanite, sillimanite, andalusite, and topaz); staurolite, tourmaline, and zircon can also be readily decomposed. Among the oxides, corundum, spinels, cassiterite, and rutil are decomposed. The sodium salts as the fusion agent are substantially more effective than the lithium salts. The metafluoroborate fusion is suitable for rapid decomposition of most rock-forming minerals. At a temperature of about 850°C, silicon is removed during the fusion by the fluoride present. Fluoride and borate are readily separated from the melt by evaporation with sulfuric acid; the insoluble residue consists of barium sulfate, tungstic, niobic acid, etc. Carbon and sulfide sulfur present in the sample are readily oxidized by the frequent introduction of air into the crucible.[558] Crucible corrosion is considerable and amounts to as much as 6.5 mg of platinum when 4 g of the fusion mixture is used.[539] The fusion is often carried out using a mixture of an appropriate fluoride and boric acid at various ratios. The decomposability of rocks[559,560] and the effect of added lithium on the subsequent determination of some cations by atomic absorption spectrometry were studied. The sodium or potassium salt of the fusion agent was employed for decomposing silicates in the determination of gallium,[561] beryllium in beryl,[562] free silicic acid,[563] and barium.[570] The mixture of fluoride and boric acid is an ideal fusion agent for uranium and thorium minerals; it readily decomposes torbernite, carnotite, and uraninite.[564,565] As it also decomposes zircon, it has been used for rocks containing this resistant mineral; after the fusion, zirconium and hafnium were determined by isotopic dilution analysis for geochronological purposes.[566] Cassiterite is easily decomposed by this mixture; otherwise, it must be decomposed by alkaline-oxidation fusion with sodium peroxide. After preliminary silicate decomposition by hydrofluoric acid, the mineral decomposition takes about 15 min; the melt is minimally contaminated by the crucible material.[567-569]

As has been mentioned,[557] this fusion agent is suitable for the determination of FeO in silicates that are not readily decomposed by hydrofluoric acid. The fusion is performed in a closed tube; the cooled melt is dissolved in sulfuric acid, and the divalent iron is determined oxidimetrically. The determination was modified for an open system and is carried out in an inert gas stream. As the solidified melt is dissolved with difficulty in mineral acids, some authors crush the glassy material and dissolve it in a known excess of an oxidant.[571] Traces of oxygen which may be present in the inert gas cause partial oxidation of the divalent iron. Carbon dioxide is not suitable as the inert gas, as it dissociates to oxygen and carbon monoxide at the fusion temperature, changing the ratio of the two iron redox forms. This procedure was used to determine FeO in gabbro, olivine, glauconite,[572] garnets, ilmenite, tourmaline, and other resistant minerals.[573,574] The amount of divalent iron found depends on the fusion time, indicating that ferric iron is reduced to ferrous during the fusion.[573,575] The reduction is probably catalyzed by platinum, which is transferred into the melt during fusion.[576] This method was used on a semimicroscale for the determination of FeO in many minerals; after completion of the decomposition, the melt is dissolved in a known amount of potassium dichromate, and the excess is determined reductometrically.[228] An interesting modification of the Rowledge procedure is fusion with fluoroborate in the presence of a known amount of vanadate in a nitrogen stream. The unreacted vanadate is again determined reductometrically.[577] The proposed procedure was applied in the determination of FeO in chromites.[462]

C. Fusion with Borates and Boric Oxide

Alkali metal meta- and tetraborates are efficient nonoxidizing fusion agents and are commonly employed for decompositions of resistant minerals. They are usually used as anhydrous salts, after dehydration at 700 to 800°C. Platinum crucibles are generally employed, but graphite ones are also commonly used. A particularly suitable material is a 95:5 alloy of platinum and gold. This alloy is not wetted by the tetraborate melt and, therefore, is easily quantitatively poured out of the crucible. After the sample decomposes, it is sometimes necessary to separate the boron added (either as boric acid methylester or as BF_3) before further analytical treatment.

Tetraborates are efficient fusing agents for oxygen-containing minerals of aluminum, iron, titanium, tin, niobium, and tantalum. The fusion is first carried out at a low temperature, then the temperature is increased to 1000°C and the fusion is continued until a transparent melt is obtained. Titanium minerals are decomposed after about 1 hr; niobium and tantalum minerals must be decomposed for substantially longer times. The melt formed is generally extracted with mineral acids; any insoluble residue which is present is separated and ignited; then the fusion is repeated. In this way, natural aluminum(III) oxide (corundum and its colored varieties, ruby, and sapphire[578]) can be decomposed, as can their synthetic equivalents. Among titanium minerals, all three natural oxides and the titanates ilmenite and perowskite can be decomposed. The fusion agent also decomposes cassiterite[579] and is suitable for iron ores containing iron oxides and silicates.[580] Tetraborates have been very successfully employed as fusion agents for natural compounds of zirconium, mineral zircon, baddeleyite,[581,582] etc. They are equally effective for oxygen-containing compounds of niobium and tantalum, chromium, and some resistant silicates, such as micas and tourmalines.[492] In this fusion procedure, fluorine is not lost during decomposition, so that the aqueous extract of the melt is suitable for the determination of fluorides after preliminary distillation.[583] An aqueous solution of the melt of silicon dioxide with tetraborate is stable for several months and, thus is suitable for preparation of silicic acid standard solutions.[584]

Alkali metal tetraborates are often employed for sample preparation for emission spectrography, X-ray fluorescence spectrometry (XRF), flame spectrometry, etc. The sample fusion essentially reduces the matrix effect if rocks of varying composition are to be analyzed; it also enables preparation of a homogeneous material and the homogenization of heavy metals added as internal standards. When melts are prepared in graphite crucibles, losses in cobalt and iron are encountered due to the process of reduction to metals.[585] Similarly, losses in copper were observed in decompositions of cupric zeolites by fusion in platinum.[316] Procedures have been described for sample preparation for spectral analysis and 5:95 gold-platinum alloy casting molds which ensure a constant cast geometry.[586-588] The Claisse Fluxer® automatic device,[589] enabling simultaneous preparation of six glasses in suitable gold-platinum alloy crucibles, is advantageous for preparation of beads and plates for X-ray fluorescence analysis. The fusion is carried out with sodium tetraborate, which is suitable for elements at higher concentrations, or with lithium salt suitable for the determination of light elements and trace concentrations of heavy elements. Barium peroxide or lanthanum(III) oxide is used as an additive in order to decrease the differences in the absorption of X-rays by various rock types. A fusion agent-sample ratio of 100:1 is sufficient for many elements at concentrations above 1%. This dilution removes interelemental effects and the X-ray intensities are proportional to the element concentrations.

This method has been used for the determination of principal and trace element concentrations in rocks,[590-593] in analyses of lunar samples,[594] and in the determination of thorium in ore concentrates[595] and silicon and aluminium in bauxites.[596] Borate melts are also suitable for direct reading spectrometers[597] and for the analysis of rocks by an electron microprobe analyzer[598] and mass spectrometry.[599] A melt solution in nitric acid was employed for the determination of lithium in silicates[600] and the alkaline earth and other elements in geochemical reference materials by AAS.[90]

Lithium metaborate is a substantially more efficient fusion agent than sodium tetraborate; it rapidly decomposes even resistant oxygen-containing compounds other than silicates (e.g., spinels, chromites, ilmenite, and others). In addition to solution analyses, the fusion agent is also frequently employed for sample preparation for X-ray fluorescence and emission spectroscopy. Keith[601] employed the fusion agent in the former method; it was introduced into analytical practice by Ingamells;[602,603] he has reviewed[604] the application of this substance in decompositions. The borate glasses obtained are mechanically resistant, not very hygroscopic, and soluble in dilute acids. The fusion is performed in platinum, gold, gold-plated platinum, gold-platinum alloy, graphite, or boron carbide crucibles. A strongly oxidizing atmosphere is required; otherwise, iron, copper, lead, cobalt, and other metals are reduced and alloys are formed with platinum. Alloy formation may lead to losses during the analysis and creates the danger of melt contamination in subsequent fusions. The platinum contents in the melt solutions indicate that corrosion of platinum crucibles by the fusion agent is negligible.[539] Gold and gold-platinum (5:95) crucibles are most suitable. Specially made glassy carbon crucibles are very advantageous for routine work. If a carbon crucible is preignited and its internal surface is not mechanically damaged, it is not wetted by the melt and the melt can easily be poured out without losses. The fusion proceeds smoothly at a suitable fusion agent-sample ratio, provided that both substances have been thoroughly pulverized and mixed together. The fusion temperature should not exceed 900°C and its duration should be 15 min; otherwise, losses of the alkalies occur. When the mixture is insufficiently homogeneous, microcrystalline silicon dioxide (insoluble in mineral acids and consequently undetected in the subsequent determination) is formed. The disadvantage of this fusion agent is that it is sometimes not available in sufficiently pure form and must be purified by recrystallization.

For the determination of elements by XRF, pellets or a button can be prepared from the crushed melt. Methylcellulose[605,606] is suitable as a binder for pellet pressing. In the preparation of buttons for XRF, metaborate is usually obtained by mixing equivalent amounts of lithium tetraborate and carbonate.[607,608]

Fusion with lithium metaborate is used in the preparation of a stock solution used in rapid silicate analysis.[609] It is also advantageous for the determination of some trace elements in rocks: a number of cations can be extracted with a liquid ion exchanger[610] after dissolving the melt in EDTA. Fusion with boron(III) oxide and lithium carbonate was employed in the determination of SiO_2 in the presence of large amounts of phosphorus, zirconium, and titanium.[611,612] The melt is dissolved in EDTA and the interfering ions are separated by ion exchange.

Sample fusion with lithium metaborate can also be used directly for the spectrochemical determination of the individual components. The pulverized melt is introduced between the electrodes using a tape machine.[613] The melt can also be dissolved in dilute nitric acid, and the rotating disk method is used for the analysis.[603] Both techniques employ spark excitation and a direct reading spectrograph. The melt can be dissolved using a suspension of a strongly acidic cation exchanger. After separation, the resin contains most of the cations from the solution; it is dried and analyzed spectrographically.[614] A new scheme of silicate analysis for 16 principal and minor elements has been developed utilizing this principle.[615]

A solution prepared from silicate and lithium metaborate melt is an ideal medium for direct determination of a number of cations by AAS. The fusion is usually carried out in a graphite crucible, and the glass is dissolved in dilute nitric acid while still hot. According to Medlin et al.,[616] silicic acid can not be determined in this way because of strong polymerization of the solution. On the other hand, this acid may be determined in the scheme[67] in a hot flame without solution pretreatment. This method of SiO_2 determination is also recommended by other authors.[615,618] There are numerous applications of the procedure in silicate analysis.[90,619-622] The fusion agent was also employed in the decomposition of fluorites and ceramic silicates.[623] With the latter, a preliminary decomposition with hydrofluoric acid, followed by fusion of the residue, has been recommended. In analyses of coal ashes containing larger amounts of magnetite, ammonium vanadate is added to the fusion mixture to ensure complete oxidation of iron.[624] Some analytical procedures are combinations of AAS and other photometric methods.[625] Materials other than rocks can also be analyzed using this procedure. This decomposition technique has been recommended for rapid analysis of copper slags[67] and for the determination of tungsten in poor ores,[626] neodymium in yttrium garnet single crystals,[627] and beryllium and vanadium in rocks.[628] Titanium-rich minerals, such as titanomagnetite, rutil, etc., can be decomposed by this fusion agent when a sufficient amount of silicon dioxide is added.[629] The melt solution is also suitable for the flame photometric determination of the alkali metals. The melt can be dissolved in dilute mineral acids[630-632] or in complexing agents, e.g., citric acid.[633,634] Lithium metaborate fused *in vacuo* can also be used for mineral fusion *in vacuo* for K-Ar dating. During the fusion, no gaseous products which would interfere in the subsequent isolation of argon and its mass spectrometric measurement are formed.[635]

Sodium metaborate is also an efficient decomposing agent. The fusion agent is usually prepared by mixing equivalent amounts of sodium tetraborate and carbonate and is used chiefly for the decomposition of resistant minerals. It has been used in analyses of zircons,[636] spinels,[637] and iron ores,[638] as well as for reliable decompositions of chromium ores and chromium-containing ceramics.[408] After the preparation of the sample solution, chromium is separated using a liquid ion exchanger, and most remaining cations are determined titrimetrically or photometrically.

Strontium metaborate is also an effective fusion agent for natural silicates. Its melting point is 1150°C, but the presence of other phases decreases this value by about 100°C. The fusion agent-to-sample ratio depends on the sample's basicity and increases from 1:5 for strongly acidic rocks up to 1:20 for strongly basic substances. A melt solution can be used to determine elements using AAS; strontium ions act as a releasing element.[639] Barium tetraborate is an energetic fusion agent for resistant minerals (e.g., corundum, zircon, etc.). The fusion agent is mixed with the sample in a 10:1 ratio and the melt is dissolved in dilute mineral acids. The solution can readily be employed for the photometric determination of the alkali metals and calcium.[640]

Boron (III) oxide, nonoxidizing fusion agent as effective as borates, is employed for the decomposition of resistant silicates and substances containing larger amounts of fluorine. This fusion agent is prepared from very pure boric acid by dehydration at 1000°C. The substance formed is strongly hygroscopic and must be stored in a tightly closed vessel. The oxide volatilizes during the fusion, especially at temperatures around 1550°C. The fusion is carried out in a platinum crucible with negligible corrosion. For the decomposition of resistant silicates (e.g., distene, staurolite, tourmalines, etc.), a five- to sixfold excess of the fusion agent over the sample is sufficient. When fusion is completed, the melt must be mechanically cracked (e.g., by repeated heating and rapid cooling) and then dissolved in dilute hydrochloric acid. In most cases, the boric acid formed must be separated as methylester. In view of the relatively high melting point, this decomposition technique is used for special purposes, such as the determination of silicon dioxide in the presence of fluoride. In order to completely remove boron trifluoride from the melt, the strongly viscous melt must be heated to 1200°C, stirring with a platinum wire.

This decomposition procedure has been used to determine uranium in rocks, where it is carried by zircon or another resistant mineral. The rock is first decomposed by hydrofluoric acid and the residue is fused with boron(III) oxide. The melt is dissolved in hydrofluoric acid and then evaporated with perchloric acid, thus removing fluoride and borate.[260,641] A fusion agent containing 10% lithium carbonate was proposed for the decomposition of silicates; the melt is dissolved in 0.1 *N* hydrochloric acid containing peroxide. The solution is used for the atomic absorption spectrometric determination of potassium.[642] Boric acid can be used for fusion instead of the oxide. The decomposition was applied to a rapid determination of silicon dioxide present at a level of over 90%. When evaporated with hydrofluoric acid, both silicon and boron oxides volatilize; the difference between the sample and residue weights yields the SiO_2 content.[643]

D. Reductive Fusion

Reductive fusion is a special procedure for decomposition of some mineral raw materials. During this procedure, the valence of the cations is decreased due to the effect of the reducing component of the fusion agent; some can even be reduced to the metals, which can then be mechanically separated from the slag obtained. The reduction product is usually more readily decomposable than the initial substance (e.g., very stable cassiterite can be reduced to metallic tin during the fusion and is then easily soluble in mineral acids).

Heavy metal oxides are readily reduced in alkaline melts, especially those of lead, copper, antimony, and bismuth. If noble metals (gold, silver, platinoids) are present in the system, various binary and ternary alloys are formed by their reactions with the fused metals. As the reduced metals have considerably higher specific weights than silicate melts, they are collected on the bottom of the fusion vessels in the form of a button, containing the entire amount of the noble metals originally present in the substance. Some platinoids are also carried mechanically into the button. This principle underlies an ancient analytical procedure called the fire-assay method, which was known as early as the second millenium B.C. and is still employed in the laboratory. A number of monographs[31,644-650] and reviews[651-656] have treated the subject. Large sample weights treatable by this procedure ensure the homogeneity of ore samples containing noble metals in the form of random inclusions; therefore, the method is employed as the standard procedure for determination of silver, gold, and the platinum metals.

The procedure consists of four steps. First, the ratio of acidic and basic components in the material analyzed must be determined in order to select a suitable composition of the fusion mixture, the main constituents of which are sodium carbonate and fused sodium tetraborate. The ratio of the substances is selected so that silicic acid in the melt is converted into an alkaline mono- or disilicate. If the material contains too much basic component, the acidity of the mixture must be increased by adding quartz or glass. Of course, the calculation must also include the amount of the effective components contained in the ore sample.[657] Sodium tetraborate or calcium fluoride is used to achieve a suitable slag viscosity. Knowledge of the redox character of the ore material is also important, as the amount of the reduced metal depends on it. Sulfides, especially pyrite, have a reducing effect; if a sulfide is present in a great amount, an oxidant must be added to modify the redox character of the ore material or sulfur (arsenic, selenium, etc.) must be removed by preliminary ignition. Large amounts of nonferrous metals, especially copper and nickel, make reducing fusion difficult; thus, it is advantageous to separate them beforehand by ore decomposition in nitric or sulfuric acid.

The pretreated sample is mixed with the fusion mixture, containing, in addition to the abovementioned reagents, a collector (usually lead[II] oxide) and a reductant, most frequently carbon or flour. The mixture is heated to a suitable temperature at which it melts, and lead(II) oxide is simultaneously reduced to metallic lead. The small beads of the reduced lead move in the melt and come into contact with the noble metals, forming an alloy. The initial stage of the fusion is turbulent and is accompanied by intense gas evolution, which stirs melt. Upon completion of the decomposition and reduction reactions, the melt becomes quiescent and the metal beads drop to the crucible bottom, where they are collected as a button. The crucible content is poured into an iron mold, is allowed to cool, and the button is removed and thoroughly cleaned. The third stage involves scorification. The button is covered with fused sodium tetraborate on a scorification dish and is heated to 950°C. All the metals, except for the noble metals, are transferred into the tetraborate melt where they form appropriately colored metaborates. Scorification can also be carried out without tetraborate; the lead(II) oxide formed serves as the fusion agent. In the final stage of the determination, the substantially diminished button is freed of lead by cupellation on a small cupel made of calcium and magnesium phosphates. The lead is partially evaporated as the oxide and partly percolates into the cupel. After cupellation, the noble metals remain as a grain at the bottom of the cupel. The grain is then analyzed for individual components. In the final stage of cupellation, it is essential that the cupel be removed when the metal bead rotating on the cupel bottom stops and lightens and then darkens (Silberblick); otherwise, part of the silver is lost.

The loss of silver during the whole fusion process was monitored using the ^{110}Ag isotope; losses depend on the total button weight and the magnitude of the silver distribution coefficient between the alloy and the melt. During cupellation a small amount of silver is lost by percolation into the cupel[658] with lead(II) oxide. A number of works have been devoted to the behavior of gold during fire assay. For the determination of its distribution during the fusion processes, radioisotopic monitoring or neutron-activation were employed. The transport of gold was monitored in all components of the system and in the devices used. It was generally found that gold deposits on the melt contact with the crucible and on the cupel underneath the metal bead.[659] Shima[659] points out the danger of incomplete Au collection caused by large contents of copper, iron, and sulfur. The accuracy of the results depends on the button size, the weight of which should be between 25 and 35 g. Copper (3 g) and nickel (0.025 g) in the button render cupellation impossible. Losses in cupellation are also caused by selenium, tellurium, and small amounts of bismuth.[660,661] The results of parallel analyses of synthetic gold-bearing ores obtained by activation analysis, by wet chemical procedures, and by fire assay indicated that the last method is most reliable. However, generally this is only true when noble metals are present in the ore in a form amenable for collection.[382] Greater loss of silver during cupellation was observed; AAS is recommended for its determination.[662] In an attempt to standardize methods and materials, lead has been recommended as a suitable collector for all noble metals. Losses in ruthenium and osmium can be compensated for by "spiking" the ore with a known amount of radioisotopes.[387] The effect of a critical amount of lead on the quantitative deposition of gold was verified[663] during the study of metal loss in dependence on its absolute amount and of the efficiency of various reductants. Too large a button requires prolonged cupellation time, leading to a greater loss of gold. Wall and Chow[664] dealt in detail with the question of losses of noble metals during the whole process under standard conditions and at controlled temperatures. The effect of the lead weight and of the Au/Ag ratio on the completeness of the separation was verified. Both of the variable components cause a constant loss of less than 1% of the gold originally present. Volatilization of the alloy during cupellation and the process of dissolution of the gold and silver grains at various temperatures and nitric acid concentrations (parting process) were further studied; it was found that losses due to volatilization are negligible, but part of the lead from the cupel diffuses into the grain during prolonged cupellation. More serious losses were observed during the fusion process; during mixing of the ore with the fusion agent on foil, as much as 1.5% of the gold was carried away in the dust. The effect of the fusion temperature can also be observed: lower temperatures lead to melts with higher viscosities; at high temperatures the melt splashed. The overall gold distribution is as follows: the grain contains 99.5%, the fusion crucible 0.7%, and the cupel 0.03%, while the slag and the solutions used for parting were free of gold.[665]

The behavior of the platinum metals during fire assay was studied analogously.[31] Statistical evaluation of the scatter of the results in the determination of the platinum metals by emission spectral analysis after fire-assay isolation of the metals, carried out in six Canadian laboratories, showed that the separation is complete. Scattering is caused by further analytical treatment.[666] Losses of iridium and other platinoids were studied by means of radioisotopes and neutron activation. It was found that losses during reduction fusion are minimal; repeated fusion of the slag leads to complete separation of iridium into the button. Considerable loss, 25-50%, occurs during cupellation; iridium was detected in the cupel material, as well as in the walls of the cupellation furnace.[667,668] The distribution of the platinum metals in the lead button was monitored using radioisotopes; it was confirmed[669,670] that iridium and rhodium cannot be concentrated in a silver grain. If lead is present, both the noble metals are protected against oxidation and volatilization; therefore, it is recommended to cupellate the button to a weight of 0.5-0.7 g and then to subject it to neutron activation analysis. The loss of the noble metals does not exceed 8%.

Collection of the platinum metals in lead is rather complicated. Added silver powder usually acts as the collector; larger amounts of nickel strongly inhibit the process. The latter must be removed by extraction with acids after thermal pretreatment of the sample. Metal sorption on the walls of the fusion crucible is a source of error in the reduction of platinum; repeated fusion of the slag is necessary.

Rhodium readily dissolves in lead, but the completeness of its separation depends on the size of the button formed. Iridium does not form alloys with lead or silver and is deposited in the button in the form of a suspension. The fusion mixture must be neutral or acidic, as it readily reacts with basic slags. Ruthenium and osmium are easily lost during cupellation, as they are readily oxidized to volatile oxides.

Thus, it is evident that the platinum metals are separated into the lead button almost quantitatively following repeated slag fusion. Substantial losses occur only during cupellation. However, the button can be used as a collector, which is then analyzed for the platinum metals by solution chemistry or by one of the radiochemical methods. Agrawal and Beamish[671] examined the distribution of the platinum metals between the button and slag during repeated basic fusion and the behavior of the platinum metals during parting with nitric acid. It was found that platinum and iridium remain almost quantitatively in the residue after acid extraction and 20% of the rhodium is dissolved, while palladium is dissolved almost quantitatively. Solubility of platinum and especially iridium in an acid increases with increasing copper content in the button.

Fire-assay preconcentration of traces of platinum metals in a lead button is often employed in determination of these elements in geological materials by emission spectrography. Haffty and Riley[672] determined the content of the platinum, palladium, and rhodium in standard rocks of the U.S. Geological Survey. They assayed the samples after adding gold as the collector. The grain obtained after cupellation was dissolved in aqua regia and the determination was carried out in solution. Gold and the platinum metals were determined in a similar material after reduction fusion without a collector.[673,674] According to Lupan et al.,[675] concentrations as low as 5 ppb of the metals can be determined in this way with an error of 20 to 40% depending on the amounts of noble metals and impurities. Iridium, ruthenium, and osmium can be separated from ores using weakly acidic fusion agents and platinum as the collector; the procedure was verified using tracers.[676]

Another method for the final determination of the preconcentrated noble metals is by AAS. Gold and platinoids can be accumulated in a silver grain after removal of lead; the grain is dissolved in aqua regia and determination is carried out.[677,678] Gold or silver are often used as collectors of Pt-metals; the amount added should be three orders of magnitude higher than the amounts to be determined.[679] In analyses of chromite concentrates[680] it has been found that no basic or acidic fusion agent is sufficiently efficient for the decomposition of these minerals; with small sample weights (3 g), the efficiency of the reduction decomposition is 90% and it rapidly decreases with increasing sample weight. An addition of 50 mg of gold must be used when iridium is to be determined in basic rocks; the detection limit is 2.5 ppm.[681] Gold, silver, palladium, and platinum can be determined by AAS after standard separation into a lead button and cupellation. The grain obtained is dissolved in aqua regia and the final solution contains KCN and EDTA.[682,683]

Neutron activation often finds application in determination of noble metals. It is possible to activate the initial material and measure the γ-spectrum of the grain after cupellation or to activate the button or grain after collector removal. The former procedure was used[684] for a highly sensitive determination of gold in rocks and for the determination of iridium in meteorites after preconcentration of the metal in 50 mg of a platinum-rhodium alloy by fire assay.[690] Traces of platinoids in rocks could be collected by gold and the grain was activated after cupellation.[685] Neutron activation analysis of the lead button was employed[686-689] in the determination of gold and the platinum metals in ores and products of affination treatment. In measurements of characteristic γ-spectra, high-resolution spectrometers with Ge(Li) detectors have been used.

Errors connected with collection of the platinum metals in a lead button during fire assay stimulated the search for more suitable collectors. Faye[656] proposed fused tin as an effective collector, as it readily forms intermetallic compounds with silver, gold, and the platinum metals. Copper, nickel, and iron dissolve simultaneously. Ore concentrates containing larger amounts of sulfur and arsenic in addition to the above elements must first be ignited and extracted with mineral acids to prevent the formation of undesirable matte and arsenides. The platinum metals transferred into the solution are reduced and joined with the insoluble residue after acid extraction. The fusion mixture consists of sodium carbonate, sodium tetraborate, quartz, tin(IV) dioxide, and coke; the fusion proceeds at a higher temperature (1200°C). After solidification the alloy formed is refused at 600 to 700°C in a nitrogen atmosphere and then rapidly cooled in water; the button cracks and can be crushed mechanically. The reduced metal is dissolved in hydrochloric acid with hydrogen peroxide and the solution is analyzed chemically. Osmium can be distilled off as the chloride and excess tin can be removed as the volatile bromide. Ion-exchange chromatography[426] is suitable for the separation of the other platinoids.

The effect of the composition of the analyzed material on the fusion process was studied systematically. Some products, such as ore concentrates, Cu-Ni-matte, and meteorite metal phases, must first be extracted in HCl-NH_4Cl mixtures. The efficacy of reductive decomposition of magnetite, ilmenite, and Cu-Ni concentrates containing platinoids as arsenides or as solid solutions in sulfides was also verified. The chemically resistant natural alloy osmiridium can readily be decomposed. Chromite is not decomposed by reduction fusion and must first be sintered with sodium peroxide.[691] Tin button is a suitable collector for silver; analyses of the slags after fire assay with a tin button indicated a residue of 0.015% of the silver originally present. After dissolution of tin button in hydrochloric acid, the dissolved silver is reduced with metallic tin, the separated precipitate is dissolved in a HCl + H_2O_2 mixture, and the silver is determined by atomic absorption.[692] According to Jones et al.[693] distillation separation of osmium from the dissolved button is unsuccessful; therefore, reduction fusion using NiS matte is recommended.

Other efficient collectors for noble metals during reductive fusion include iron and nickel alloys. Both metals are present in sulfide concentrates in substantial amounts; the fusion mixture contains sodium carbonate and sodium tetraborate, and a graphite crucible or added graphite acts as the reductant. The reduction occurs at 1350°C. A maximum amount of the alloy is formed within 15 min after attaining this temperature. The quiescent melt consists of three phases: the alloy, a sulfidic matte, and slag. The matte formed contains only trace amounts of platinum and 5% of the total amount of palladium; however, its formation can be prevented by preliminary combustion of the sulfur. The fusion is important chiefly for isolation of the platinum metals which are often bound to ferrous-nickel(II) sulfide. The presence of nickel leads to considerable losses of the platinum metals in classical fire assay using lead. On the contrary, collection on an alloy has proved successful in the determination of platinum, palladium, and rhodium in sulfide concentrates and in the determination of osmium and ruthenium. Although the solubility of iridium in the alloy is somewhat limited, the alloy still contains up to 95% of the metal present. The fusion is suitable even for the decomposition of resistant materials, such as natural alloy osmiridium.

Alloys of iron, nickel, and copper are also collectors of the platinum metals.[694] They are suitable for isolation of all platinum metals, including osmium.[695] The processs of collection of noble metals was verified by evaluation of a noble metal-bearing ore standard.[387] A copper button[696] was proposed for separating rhodium in the presence of larger amounts of copper. Copper forms several defined compounds and a number of solid solutions with rhodium. The fusion proceeds at 1200°C and is very efficient for traces of rhodium. Losses of the metal into the slag and the crucible walls are usually less than 4%.

Nickel(II) sulfide is also suitable as a collector of the platinum metals. Fusion yielding this button is very universal and is virtually unaffected by the sample composition. The fusion mixture consists of sodium carbonate and tetraborate, nickel(II) carbonate or oxide, and an equivalent amount of sulfur. If the materials analyzed are very basic, quartz is added. The fusion temperature lies between 800 and 1000°C. The slag formed is not very viscous and contains no NiS. The fusion mixture is used in a threefold excess over the sample and the slag must be repeatedly fused. The main parameters of the fusion,[697,698] the temperature and its duration, the effect of the matrix, and the effect of the button size and excess sulfur on the platinoid recovery were verified. During fusion, noble metal sulfides and transition metal sulfides form the button. Sulfides are very suitable collectors for the platinum metals, but the results for gold are markedly scattered. Advantages of the procedure include the low fusion temperature and the fact that thermal and chemical sample pretreatment is generally not necessary. The matte is sufficiently heavy and is easily pulverized mechanically. The subsequent extraction with acids is very easy. Difficulties are encountered in the fusion if the material contains too much iron and copper. If iron and copper sulfides comprise more than 10% of the sulfide present, another sulfide phase is formed, causing losses of noble metals in the slag.[703] The decomposition efficiency was checked using radioisotopes,[667,668,699] and a comparison was made with other fire-assay procedures.[387,700] The procedure was employed, among other applications, for the decomposition of osmiridium[701] and for other platinum-bearing raw materials.[693,702]

Reductive fusion is only rarely used for the determination of metals other than the platinoids. One example is reductive fusion with potassium cyanide, employed for the decomposition of tin(IV) dioxide (cassiterite). Similar effects are achieved by fusion with sodium carbonate and finely dispersed carbon. If the melt does not come in contact with air, the reduced tin separates on the crucible bottom. The reduced tin can be converted into an alloy with copper, which is added to the fusion mixture as the oxide.

Other examples of systems suitable for reductive fusion include mixtures of alkali hydroxides with metallic sodium or zinc or a mixture of sodium hydrocarbonate with aluminum and carbon.[704] The former was employed for the decomposition of cassiterite; the latter can quantitatively reduce sulfate to sulfide. For determination of sulfur in coal by reductive fusion, reduction of sulfur compounds to sulfide with fused alkali metals or metallic magnesium was proposed.[705]

Silicates which are fused with difficulty (e.g., tourmalines) can readily be decomposed by fusion with a mixture of sodium hydroxide and aluminum powder. Following mild heating, an exothermic reaction starts and the mineral decomposes within several minutes.[706] Magnesium powder was employed for decomposition of a silicate mixture in the determination of the sum of alkali metals. The reaction mixture is extracted with 50% ethanol and the alkali hydroxide liberated is determined by alkalimetric titration.[707]

To determine total iron in silicate ores (which are difficult to decompose in acids), Quadrat[708,709] recommended a fusion mixture containing sodium carbonate and potassium oxalate (5 + 1). When heated, carbon monoxide is formed by oxalate decomposition and reduces part of the trivalent iron to divalent, thus facilitating rapid decomposition of silicates by the alkaline fusion agent.

E. Alkaline Fusion is the Presence of Sulfur

This type of fusion, also called Freiberg decomposition, is suitable for decompositions of sulfidic raw materials containing arsenic, antimony, tin, and molybdenum. During heating, an alkali polysulfide is formed from a mixture of sodium or potassium carbonate and sulfur, which reacts with a number of elements yielding sulfides and sulfosalts. Undissolved sulfides can then be separated from soluble sulfosalts by extracting the melt with water. The ratio of the fusion agents is selected so that all sulfur is bound by the alkali metal present. Porcelain crucibles are used for the fusion. The analyzed sample must be very finely powdered and thoroughly mixed with an 8- to 15-fold excess of the fusion agent. An alkali sulphide is formed during first stage of the fusion, which takes place at a low temperature. At a higher temperature, the decomposition itself and the formation of a polysulfide occur; the temperature must then be decreased slowly. Ferrous, nickel (II), and cobalt (II) sulfides tend to form colloidal solutions; the melt extract must then be heated in a water bath, adding potassium or ammonium chloride. Copper and mercury form soluble sulfosalts in the presence of excess sodium ions and appear in both phases; the formation of these compounds can be prevented by using potassium salts. With rich mercury ores, the sulfide recovery is not quantitative due to metal volatilization during the fusion.

Freiberg decomposition has been used in the analysis of separated minerals, rich ores, and concentrates. The simple separation of sulfosalts from sulfides considerably simplifies the analysis. The decomposition has been applied to lead sulfoantimonates, bournonite, boulangerite, jamesonite, and other minerals of this group. Noble silver ores, miargyrite, pyrargyrite, proustite, and sulfostannate stannin can also be decomposed, as can germanium minerals. The procedure is advantageous for the separation of antimony[710,711] from polymetallic ores, bismuth from excess arsenic, and molybdenum in the analysis of bismuth ores. The fusion has also been used in decompositions of cobalt and nickel arsenides from the safflorite-skutterudite group. During the decomposition of a copper concentrate by a mixture of potassium carbonate and sulfur, copper can be quantitatively separated as the sulfide and antimony can be determined in the extract polarographically, photometrically, or by atomic absorption.[712,713] The loss of antimony has been observed in materials containing large concentrations of silicon dioxide; this is probably caused by sorption of antimony on the silica gel formed.[282]

Tetrahedrites are important members of the sulfosalts mineral group. They are economically important sources of copper, silver, and mercury. Their complete analysis can also be effectively carried out using the Freiberg decomposition.[714,715] A rapid determination of antimony in a flotation tetrahedrite concentrate and in thermal treatment products has been described.[713,715]

Small amounts of cassiterite can also be decomposed by fusion: the decomposability of this mineral probably depends on the amount of heterogeneous inclusions. Alkaline fusion in the presence of sulfur was proposed for the determination of tin in rocks and poor ores.[716] However, determinations of this element in galenite and other sulfides have indicated that the separation of the sulfostannate from separated sulfides is not quantitative,[717] as losses in tin amounted to as much as 50%.

V. SAMPLE DECOMPOSITION BY SINTERING

As fusion decompositions always lead to substantial contamination of the analyzed material by introduction of salts and trace elements and/or by crucible corrosion, attention has been centered on decompositions in which the amount of the fusion agent is limited to the necessary minimum. Such procedures are called sintering; during the decomposition, the mixture is not fused by sintered and the reaction of the mixture with the vessel material is minimal, because of the low temperature used. The residue formed can usually be readily removed from the crucible and is generally easily soluble in mineral acids. The completeness of the decomposition depends on the reaction conditions, i.e., the decomposition mixture composition and its amount, the heating gradient, and the heating time. These conditions are usually determined empirically for each analyzed material.

Sintering involves solid state reactions, i.e., the reactants and the products are solids. The reaction mechanism is assumed to involve the formation of a monomolecular layer of the reaction product at the interface of two crystalline solids. Particles constituting the crystal lattice oscillate with a higher energy with increasing temperature. Therefore, when a mixture of crystalline powders is heated, ions or molecules can overcome the lattice forces due to their increased oscillation amplitude and can exchange their positions. The exchange probability is, of course, very low for particles in solids with ideal crystal lattices. The temperature at which this initial exchange starts marks the beginning of internal diffusion, which then continues at a measurable rate. It has been found that the absolute initial temperature of internal diffusion is 57% of the absolute fusion temperature for some salts. The reaction products are transported by diffusion from the interface and the reactants again come into contact and react. This diffusion corresponds to very slow stirring of the solid reaction mixture. Reactions among solids thus proceed very slowly and usually are not completed during the experiment. The substance activity may simultaneously depend on the preparation procedure, the presence of a gaseous or liquid phase, distortions of the crystal lattice, the presence of other compounds, and ion polarization. For example, the recovery of magnesium chromite formed by reaction of ferrous chromite with magnesium oxide is lower at the same temperature than with a mixture of chromite and carbonate. When using carbonate thermal decomposition, a much more active oxide is formed than with an oxide whose lattice is ordered by ignition. An increase in reactivity due to distortion of crystal lattices has the same basis. Active oxides, prepared by dehydration of hydroxides, react more effectively than oxides prepared by prolonged ignition, as the crystal lattices of the former are expanded or distorted.

The reactivity of solids can be affected by the presence of some gasses, although there is no reaction between the gas and the solid. The gas may penetrate into the crystal lattice and dissolve in the substance, changing its reactivity. For example, sulfur trioxide decreases the quartz activity, while sulfur dioxide and oxygen increase it. A change in the activity has been observed in syntheses of calcium silicate from the oxides. Other contaminants capable of forming solid solutions or intermediates with the reactants have similar effects.

Reactions in the solid phase occur much faster in the presence of a liquid phase, not only due to hastening of diffusion processes, but also due to the considerable increase in the interface area, as the reaction surface then equals the total surface of the solid particles. The reaction surface is often liquid; then, a liquid product layer is formed at the interface of the crystal lattices, and its thickness increases in time. The course and rate of the reaction are then determined by the mode and velocity of the reactant particles through this layer and by the reaction rate at the interfaces where the reactant crystal lattices are destroyed. During sintering, the reaction rate is increased by even minute amounts of a liquid phase: the layer of the powdered mixture is not fused, but is sintered into a solid agglomerate.

The rate of reaction between solids can be increased by adding substances which cause the formation of eutectic melts. The reaction heat liberated usually suffices for heating the mixture to the temperature required for fusion of the reactants or for heating their eutectic mixtures with the newly formed compounds. The solid state process is only the initial reaction stage; it is slow, but is hastened during formation of a liquid phase.

If solid solutions are not formed among the reactants and the products during the reactions of solids, the activity of all components remains constant throughout the reaction. Hence, these reactions cannot attain equilibrium. The reaction is terminated when the reactants are consumed. Reactions in the solid phase proceed in the direction of decreasing free energy of the system. If only solids participate in the reaction, the entropic change is small and can be neglected in practice. Therefore, the direction of these reactions is determined by diminishing the enthalpy; solid state reactions are always exothermic.

A. Sintering with Sodium Carbonate

The decomposition of silicates by fusion with excess sodium carbonate causes an enormous increase in the sodium ion concentration and thus creates unfavorable conditions for subsequent determination of the individual elements (e.g., for chelatometry and most flame photometric determinations) and hinders the separation of silicic acid. However, the amount of salts can be decreased by using sintering. This decomposition, proposed by Finn[718] and developed by Hoffman,[719] has recently been verified for series application. The sintering is carried out in a platinum crucible with a 1.5 to 2-fold excess of sodium carbonate containing 10% sodium nitrate. The sintering temperature should not exceed 780°C; its duration (30 to 180 min) depends on the chemical nature of the compounds subjected to decomposition. The aggregate formed is readily soluble in hydrochloric acid. The study of decomposability of monomineral fractions has shown that the decomposition is as universal as fusion; most rock-forming minerals, quartz, feldspars, micas, pyroxenes, and amphiboles are smoothly decomposed. Accessoric components, such as tourmaline, garnets, axinite, zeolites, and foids, can also be readily decomposed. Zircon and aluminum silicates (e.g., cyanite etc.) remain unattacked. X-ray patterns of the sintering products indicate that a new product was formed during the decomposition; the determination of the CO_2 released corresponds to 99.0 to 99.9% completion of the decomposition reaction.[721] The undecomposed residue contains mainly aluminium oxide. The decomposition has been verified many times using standard rocks[720] and has been introduced in the laboratories of some geological surveys. Acidic rocks (e.g., granite, gneiss, or greisen) are decomposed after as little as 20 min heating, while basic rocks (such as basalts, serpentinites, and gabbros) require longer decomposition times (up to 3 hr). Even beryl can be decomposed by sintering at 1000°C. For successful decomposition, the material must be finely powdered and thoroughly mixed with the reagent, as by pulverizing the mixture on an agate mortar. Crucibles made of any material which is not fused at the given temperature can be used in addition to platinum crucibles.

If enough air comes into contact with the sintered mass, sulfide sulfur is quantitatively oxidized to sulfate, and tellurides and selenides yield soluble compounds of the tetra- and hexavalent elements. The sulfide of tetravalent molybdenum (molybdenite) can be completely oxidized with formation of sodium molybdate and sulfate.[722] This decomposition procedure has been recommended for the determination of phosphate in a molybdenite concentrate.[723]

Certain chromites[724] and iron and aluminium oxides (bauxites)[723] can also be decomposed. This procedure is also effective for rapid analysis of oxidic iron ores; the decomposition is carried out at a higher temperature (1000 to 1100°C) for 1 min. It has been prescribed as a standard method because of its universal character.[725] Boron bound in coal ashes can be converted into an alkali borate by sintering at 950°C for 15 min. The coal is combusted with sodium carbonate at 500°C for 24 hr prior to the sintering.[726]

B. Sintering with Sodium Peroxide

Application of the strong decomposing effect of sodium peroxide is limited by its strong corrosive effect on the crucible material. However, thermal study of decomposition reactions with this substance has shown that numerous resistant minerals can be decomposed by peroxide at low temperatures. Most mineral phases can be sintered with peroxide in a platinum crucible; the corrosion of platinum is negligible,[727] provided that the material does not contain sulfides and the temperature does not exceed 500°C. A fourfold peroxide excess suffices for the decomposition of most minerals and rocks. The crucible with the analyzed mixture is placed in an oven at a controlled temperature and is heated for 7 to 8 min; it is then removed and cooled. In this manner, numerous minerals and ores, including magnetite, gypsum, celestine, wolframite, scheelite, titanite, quartz, feldspars, micas, clay minerals, etc., can be reliably decomposed. Even resistant minerals, such as zircon, rutil, ilmenite, cassiterite, and chromite, are decomposed. For rocks, the decomposition of basalts, trachytes, andesite, and granites was verified. A detailed thermal study showed that a majority of rock-forming minerals are decomposed at temperatures from 250 to 300°C; the decomposition involves an exothermic reaction. With resistant minerals, an endothermic reaction is first encountered, which is an approximate criterion of the mineral stability. Rafter[727] quantitatively recorded the amount of oxygen released during decomposition and, from this information, derived the reactions taking place in various phases. Resistant minerals (e.g., beryl, ilmenite, and rutil) must be sintered with a larger reagent excess and the duration of heating must be extended to 15 to 30 min.

The decomposition of mineral silicate materials by sintering with peroxide was evaluated.[534, 721, 728, 729] The material should be finely powdered and thoroughly mixed with dry peroxide; this process is similar to sintering with sodium carbonate. Small sample weights (20 to 100 mg) and a longer heating time have been recommended[728] for silicate decomposition. Under the given conditions, decompositions with a mixture of sodium peroxide and hydroxide (3 + 2) can be performed in a platinum crucible. The mixture is effective particularly for the decomposition of resistant minerals and silicates with high contents of ferrous oxide. The balance of the iron and platinum distribution between the sintered aggregate and the crucible walls is more favorable than in fusion with sodium carbonate. Sintering has been successful in decompositions of thorium-bearing, rock-forming, resistant minerals (e.g., zircon, thorite, euxenite, and black sands). This decomposition procedure is frequently employed for these purposes.[730-732] However, it has been observed that acid-insoluble thorium compounds[733] are formed during leaching of the residue with water. It has been recommended[554] that the extract be filtered off and the residue decomposed by fusion with fluoride.

Zircon or rutil alone can be decomposed by sintering with peroxide in a platinum[734] or glassy carbon crucible.[636] As traces of platinum in the solution may interfere in the determination of thorium, iron crucibles were also recommended for zircon decomposition.

Sintering with peroxide can also be successfully employed to isolate gold and platinum metals. It has been used in analyses of rocks from Witwatersrand,[735] ore concentrates, chromites,[691] and residues after extraction of mattes[504] containing platinum metals. Alimarin et al.[736] studied the decomposition of natural materials by sintering with peroxide to determine ruthenium and osmium content. Both metals pass into an alkaline extract of the aggregate. Using radioisotopes, it has been found that as much as 25% of the two metals is lost through adsorption on the walls of nickel and iron crucibles during the decomposition of silicate materials by sintering with peroxide at 500°C for 100 min; no loss has been observed with sintered corundum crucibles.

Sintering with peroxide is a reliable decomposition method for resistant chromites, as is fusion; it has been used for complete analysis of separated mineral fractions,[411] as well as chromium ores and ceramics.[408] According to

Bouberlová,[737] the decomposition of cassiterite by sintering with peroxide is complete, but sometimes only 90% recovery or less has been attained; this is in accordance with our previous experience. It seems that mineral reactivity is closely connected with the amount of isomineral elements in the lattice and heterogeneous contaminants. A spectrophotometric determination of tin in rocks after this decomposition procedure has been described.[738] In technological practice, sintering with peroxide is also employed for the decomposition of phosphate raw materials, iron and manganese ores, slags, and foundry sands. Decompositions of sulfides are rarer, as the platinum crucible must be protected against corrosion by a layer of fused sodium carbonate or sulfate.

C. Sintering with a Mixture of an Alkali Carbonate and a Metal Oxide

For sintering decomposition of sulfides, oxides, silicates, and solid caustobiolites, a mixture of an alkali carbonate and a divalent metal oxide (magnesium, calcium, and zinc) is often employed. The composition of these mixtures is mostly empirical, depending on the character of the analyzed material. Metal oxides react predominantly with silicic acid and some volatile oxides to form sparingly soluble salts; they also act as a lightening agent. Sodium carbonate forms a weakly alkaline medium and contributes to the formation of aluminates and carbonates. Sintering can be carried out in a platinum or corundum crucible; porcelain crucibles often suffice, as well.

A mixture of sodium-potassium carbonate and magnesium oxide is the Steady alkaline fusion agent; a similar mixture with MgO predominating is the Eschka mixture. The former is suitable for decompositions of fireproof steel mill ceramic materials and chromites. Chromium is oxidized to chromate during the decomposition and can be separated from the other elements by extraction with water. The Eschka mixture is frequently employed for the decomposition of sulfides, polysulfides, and sulfosalts. Sulfur is oxidized to sulfate during heating; selenium also yields soluble selenite, while the analogous tellurium compound remains quantitatively in the insoluble fraction.[739] The Eschka mixture with an oxidant added is suitable for the determination of sulfur, arsenic, and germanium in bitumens and coal.[740] After sintering of rocks with a mixture of sodium carbonate and MgO (4 + 1) at 900°C, chromium, molybdenum, and vanadium pass quantitatively into the aqueous extract of the aggregate and can be determined photometrically;[741-743] halides are also extracted and can be determined.[744,745] For the determination of iodine, it is necessary to decompose in a nickel crucible. The Eschka mixture containing metallic zinc can also be employed for an indirect iodometric determination of sulfur in sulfides and their concentrates.[746]

In some sintering procedures, magnesium oxide is replaced by calcium oxide or caustic lime. The increased basicity of the mixture is particularly useful in decompositions of chromites. During heating, iron and chromium are oxidized to higher valence states. Spinels of the type $Ca(Fe,Cr)_2O_4$ are formed as intermediates and finally lead to the formation of chromates; fireproof silicates (e.g., sillimanite and mullite) can be decomposed equally well.

A mixture of sodium carbonate and zinc oxide has been used widely in sintering decompositions. Zinc silicate formed during decomposition of minerals has low adsorptive activity, and is a suitable substance for the separation of silicic acid from many elements.

The mixture is very frequently employed for the determination of sulfur in sulfides, carbonates, and silicates; this decomposition procedure is recommended as standard. Sulfides are oxidized to sulfates and baryte is partially decomposed, while less stable natural calcium and iron sulfates are decomposed completely. Selenium, contained in the analyzed sulfide minerals, can also be oxidized in the same way and passed into an aqueous extract of the aggregate.[740] Minerals of arsenic and antimony, sulfides, oxides, or arsenides are readily decomposed by sintering with this mixture. Arsenic passes into the extract in the form of arsenate ion.

The decomposition mixture is an ideal reagent for decomposition of a great majority of rock-forming silicates and is applicable chiefly to rapid isolation of halides and boric acid; the decomposition is very rapid and complete. The distribution of certain elements between the aggregate and the water extract was studied;[747] for subsequent boron determination the dissolved alkali carbonates and aluminates can be decomposed by a solid cation exchanger. In the extract, boron and halogenides are determined titrimetrically, photometrically, or by ion-selective electrodes.[748-754] The method of silicate decomposition and subsequent determination of halides has been verified many times using standard rocks, lunar materials, meteorites, etc. The results of the determination are in excellent agreement with those obtained after distillation or pyrolytic separation.

This decomposition procedure has also been employed for the determination of silicon dioxide in silicates with a high fluorine content.[755] Among other anions which can be separated by passage into the extract, molybdenum and vanadium should be mentioned. The procedure has been recommended for the determination of molybdenum in copper concentrates.[756] Phosphate ions do not completely pass into the extract; some of it is retained in the precipitate, probably as basic ferric phosphate.

The sintering mixture can be modified by adding further reagents. After adding magnesium carbonate, it can be used for the determination of total sulfur in rocks[721] and fluorine in silicates.[757] The addition of sodium tetraborate improves the decomposition of chromite.[758] Sintering with a mixture of sodium carbonate and calcium oxide or barium carbonate and calcium oxide has yielded good results in the decomposition of titanium, zirconium, niobium, tantalum, and other borides.[759]

A mixture of sodium carbonate, nitrate, and chloride was used for the decomposition of wolframites.[760] Beryl can be decomposed by heating with fluorosilicate; fluoroberylate can be separated in the extract from sparingly soluble aluminum and iron fluorides.

A mixture of iron powder and zinc oxide serves for reductive sintering of sulfur-containing ores, especially cinnabar. Ferrous sulfide is formed by the thermal reaction, while mercury is distilled off quantitatively. A layer of copper filings and magnesium oxide is used[761] for complete deposition of arsenic and antimony. Sintering mixtures containing calcium oxide and nitrate or magnesium oxide and calcium hydroxide have been proposed for quantitative combustion of coal in the determination of arsenic and germanium.[762,763]

D. Decomposition by the Method of J. L. Smith and Sintering with Metal Oxides

A classical decomposition of silicates for the determination of alkalies is based[764] on sintering with calcium carbonate and ammonium chloride. Calcium oxide, which is formed during the decomposition, is highly reactive and gives rise to insoluble silicates, borates, phosphates, and sulfates. On thermal dissociation of added ammonium chloride, hydrogen chloride formed reacts with the alkali metals. An advantage of the decomposition, compared with solution procedures, is perfect separation of magnesium. A very finely pulverized sample thoroughly homogenized with the sintering agent is necessary for complete decomposition. The method of J. L. Smith is generally employed for decomposition of rocks; acidic rocks are decomposed rapidly, while basic ones require several hours of treatment. Aluminium silicates, andalusite, cyanite, and topaz are among the poorly decomposable minerals. Magnesium micas, staurolite, beryl, chlorites, and some garnets are also decomposed with difficulty. On the other hand, alumosilicates, especially feldspars, and minerals with higher contents of ferrous iron are readily decomposed. Crystal lattice contraction during iron oxidation contributes to more rapid destruction of the mineral.

It is advantageous to release sodium and potassium from the silicate lattice by the above-described decomposition technique; this procedure is unsuitable for isolation of the other alkali metals. The decomposition method now has only historical value and it has been replaced by decompositions with acids. An interesting modification is the decomposition of silicates under pressure, using the Smith mixture.[631] The pellet formed is directly atomized in an acetylene-air flame in the AAS determination.

Ignition of silicate materials with calcium carbonate or oxide is similar to the procedure of J. L. Smith. Calcium monosilicate is formed by reaction with the active oxide and is readily soluble in mineral acids. The procedure has been used for decomposition of aggregates and cement raw materials,[61] silicates, and glasses[765] and for the determination of fluorine in coal.[766] This sintering also produces rapid and selective release of rhenium from natural materials. The decomposition is hastened by the presence of an oxidant, usually potassium permanganate. Tetravalent rhenium, present mostly as the sulfide, is oxidized to heptavalency during the decomposition and forms calcium perrhenate soluble in water. On the other hand, molybdenum that carries rhenium yields water-insoluble calcium molybdate; arsenic, selenium, and tellurium yield water-insoluble salts, thus enabling simple separation of rhenium by extraction.[767] A number of applications have been described for the determination of this element in molybdenum and copper minerals, and their dressing products.[768-770] Magnesium oxide combined with an oxidant has similar effects and has been used for the same purposes.[771,772]

VI. SPECIAL DECOMPOSITION PROCEDURES

A. Thermal Decompositions

Physicochemical processes taking place in minerals during heating fall into two groups: (1) Release of volatile material components in the air, in a controlled atmosphere or *in vacuo*. Oxidation or reduction of some elements and thermal dissociation of compounds may also occur. (2) Structural changes occur during heating, accompanied by formation of new phases, incongruent fusion, or (in the presence of decomposition agents) reactions in the solid state. The phases formed are generally easier to decompose than the original material.

Moisture and bound water are most frequently released from minerals during ignition, which is carried out in a tube through which a dried inert gas passes and transports the water vapors into an absorption system. The other manner of decomposition consists of various modifications of the Penfield procedure, based on sample ignition in a closed system without a carrier gas.[8] Water then condenses[773] on cool places in the decomposition tube. The decomposition can be carried out either by heating to a high temperature[774] or by adding suitable fusion agents which decrease the substance melting point; the fusion agent also binds sulfur and halogens and prevents water decomposition by ferrous iron at high temperatures. Lead(II) oxide, calcium tungstate, and lead(II) chromate are used as fusion agents.[218] A mixture of oxide and chromate or magnesia and lead dioxide yielded good results for minerals fused with difficulty.[775] The water deposited can be determined gravimetrically or by titration with the Karl Fischer[774] reagent or conductometrically and coulometrically.[776] For the determination of deuterium oxide, the water deposited is decomposed by metallic uranium and the resultant gaseous mixture is analyzed by mass spectrometry.[777]

Rock fusion *in vacuo* is used to isolate gaseous inclusions and gases retained in the crystal lattice. The combustion oven is usually combined with a device for separation of the gases released from water; the whole system is maintained in a high vacuum. High-frequency radiation[778-780] is generally used for heating. The decomposition is effective for isolation of radiogenic argon in absolute dating and analysis of gaseous components of rocks and minerals.[779-781] Mass spectrometry is most frequently employed for the final determination; gas chromatography is used less frequently. Interpretation of nitrogen bonding in rocks is difficult; it is usually present as ammonia, either as a component of minerals or due to a reaction between hydrogen and nitrogen.[249,782] Oxygen in coal is determined by vacuum pyrolysis.[783]

When ignited at a defined temperature, organic substances can be destroyed and converted to elemental carbon or carbon dioxide. The temperature selected by convention for differentiation between organic and carbonate carbon is 550°C.[784,785] However, some sulfides catalyze the decomposition of siderite and magnesite below this temperature.[786] Electronic low-temperature ashing[787] was developed for mineralization of bituminous coals. Organic compounds can be combusted readily in an oxygen stream with a slow increase in the temperature or in the presence of catalysts.[788,789] Most carbonates dissociate quantitatively at 1100°C; only barium and strontium carbonates require higher temperatures.[249]

Sulfide sulfur can be combusted to a mixture of oxides in an oxygen stream or using catalysts. Vanadium(V) or tungsten(VI) oxides are suitable catalysts.[790-792] Induction heating is advantageous and has been employed in the determination of sulfur in soils, rocks, and ores.[793] In an induction furnace, the sample is combusted in an oxygen stream at 1450°C in the presence of metallic tin or iron powder; the latter yielded better results.[794] Sulfur in sperrylite,[795] rocks, and iron ores can be determined in this way. There are also automatic sulfur analyzers, such as Leco®, etc. Sulfur in coal can be oxidized with oxygen in the Parr autoclave to form sulfuric acid, which is then titrated.[796]

Traces of tellurium in rocks can be separated by heating the sample with pyrite. Tellurium condenses with sulfur on colder parts of the apparatus[797] or can be deposited in graphite, which is then used for spectrochemical determination.[798]

A number of other compounds volatilize during thermal decomposition of materials. In analytical chemistry, separation and deposition of mercury are at present most important, followed by determination, usually by AAS. The sample is heated either alone or with a fusion agent in an air stream; the mercury vapors are deposited on a gold foil[799-802] or are freezed-out.[803] The isolated mercury is released from the amalgam by heating and its vapors are determined by AAS. This principle has been utilized in a number of commercial mercurometers. Coal can be combusted at a lower temperature in an oxygen stream and mercury can be absorbed in a $KMnO_4$ solution.[804]

The behavior of tellurium during combustion of organic materials was studied by Bock.[304] If the substance is heated with added magnesium oxide and nitrate, no loss occurs. The behavior of 14 elements during a 3- to 24-hr heating period (at 400 to 900°C) was studied using radioisotopes.[805] There are losses through adsorption on the combustion vessel (Pb, Cu, Zn) or by volatilization (Fe, As, Sb, Au, Hg). The behavior of arsenic[806] during sediment combustion or of gold during the ignition of sulfidic ores[378] was further studied. Amounts as small as a nanogram of lead can be separated[249,807] from rocks by sublimation *in vacuo* or in a nitrogen stream at a high temperature. Trace concentrations of thallium, bismuth, cadmium, indium, and zinc can be preconcentrated from these materials by selective evaporation and determined after dissolution of the sublimate.[49,808]

Heating is sometimes successful in destroying the crystal lattices of stable minerals containing bound water, thus preparing a phase more readily soluble in mineral acids. After brief ignition at 700°C, kaoline, bauxite, silicate iron ores containing ferrous chlorites, and many clay minerals which are component parts of cements[809-811] can be decomposed in hydrochloric acid. On the other hand, more intense ignition of these materials leads to insoluble aluminosilicate mullite. When heated at the above temperature, vesuvian is converted into a soluble form,[812] while all the cesium can be extracted from pollucite[813] after heating the mineral at 200°C. Carbonate dawsonite[814] is converted into alkali-soluble sodium aluminate when heated. For differentiation between ilmenite and titanosilicates, ignition at 800°C is recommended. Ferrous iron of ilmenite is oxidized to hematite and titanium is separated as the resistant oxide.[815] By igniting chromite first in a stream of nitrogen and then in oxygen, the increase in the oxygen content, proportional to the divalent iron content, can be determined. The method is more reliable than common fusion with vanadate and metafluoroborate.[462] Calcium fluoride and barium sulfate can be readily decomposed[816,817] by heating with silicon dioxide. Ignition of the latter *in vacuo* at 1400°C yields sulfur dioxide and oxygen, while barium oxide reacts with quartz to form a silicate.

B. Decompositions of Minerals by Heating with Ammonium Halides

Ammonium salts of various acids are suitable fusion agents; their melting point is low and, except with fluoride, the decomposition can be performed in glass vessels at Bunsen burner temperatures. Their acidic character, given by the dissociation of an active hydrogen atom during thermal decomposition, makes ammonium salts suitable for reaction with basic oxides and sulfides. Reactions of ammonium iodide with antimony and tin compounds are especially effective. Volatile iodides are formed during the decomposition and sublime from the reaction mixture. This simple decomposition was first used in geochemical prospection for tin[818,819] in soils and sediments. It was later modified for quantitative determination of tin in cassiterite ores and concentrates;[820,821] the effect of the amount of fusion agent, temperature, and fusion duration upon decomposition completeness was studied. The procedure has been used to determine small amounts of tin in rocks[822,823] and poor ores.[824,825] Sulfur compounds of tin can readily be decomposed by this reagent; certain kinds of cassiterite (stream tin and wood tin) are attacked by the iodide only after preliminary extraction with hydrochloric acid, which removes secondary layers of iron oxides from the mineral.[64] This decomposition technique is not quantitative for greisens, as the tin bound in silicates is not liberated by the iodide. A simple separation procedure has been developed for differentiation of tin bonding: after rock decomposition by hydrofluoric and nitric acids, part of the insoluble residue is heated with ammonium iodide. All of the tin is contained in the sublimate. The remaining part of the insoluble residue is treated with hydroiodic acid, which dissolves fresh tin dioxide formed from the silicates, but not cassiterite.[185] Cassiterite can also be separated from tungsten minerals by sublimation. Generally, the decomposition temperature is between 400 and 500°C; finely pulverized analytical samples are required. Mechanical devices have been constructed for series analyses, ensuring complete decomposition and deposition of the sublimate.[826,827] The tin in the extract of the decomposed matter is most frequently determined by AAS.[64,820,823-825]

An analogous decomposition and determination of antimony in soils and geological materials was proposed,[828] and the efficiencies of various decomposition procedures were compared. The proposed procedure was applied to the determination of antimony in ores[829] and concentrates;[830] the optimum decomposition conditions, the reagent amount, temperature, decomposition duration, and the grain size of the analyzed material were determined. It has been pointed out[831] that the analyzed mixture must be thoroughly dried in order for the decomposition to be incomplete. After dissolution of the sublimate and the residue in mineral acids, antimony can be determined by AAS in extract[828,829] or in an organic phase obtained by extraction of the antimony complex with trioctylphosphineoxide in isobutylmethyl ketone.[831]

Antimony and tin minerals can also be decomposed by heating with ammonium chloride. The chlorides formed are dissolved in hydrochloric acid, and the determination is carried out[832,833] in the solution. For decomposition of tin ores and concentrates, a mixture of zinc powder with ammonium chloride (1 + 2) was proposed; the decomposition takes place at a higher temperature than with the iodide.[704] Natural carbonates can be converted into chlorides by the effect of ammonium chloride at increased temperatures; an aqueous extract is then used in subsequent analyses.[834] The use of NH_4F and NH_4HSO_4 is mentioned in Sections IV.B.1 and IV.B.2.

C. Decompositions in Gas Streams

Decomposition of inorganic materials in a gas stream is often a very effective method of treating the analyzed mixture. Some gases can convert the substances originally present into more easily decomposable compounds. Some elements react with gases to produce volatile compounds, thus combining separation with decomposition. The original sample is separated into the following parts: a residue in the boat (resistant toward the gas employed), a sublimate depositing on cold parts of the reaction tube, and gaseous products. Advantages of using gases for decompositions include that they can be obtained in a very pure form and the minimal possibility of contamination, compared to other decomposition techniques. Therefore, this procedure may be useful in determining micro and ultramicro amounts of elements.[233,490]

The reducing effect of gaseous hydrogen at an elevated temperature can be used in the reduction of some oxides, such as cassiterite, which is readily reduced to metallic tin;[835] the metal is then easily dissolved in hydrochloric acid, while the original mineral can be decomposed only by energetic alkaline-oxidative fusion. The procedure was also employed in the separation of tin from wolframite and columbite-tantalite concentrates.[836]

Bi- and trivalent iron oxides, major components of various iron ores, can be quantitatively reduced to the metallic iron by hydrogen at 600°C. The varying reducibility of iron silicates has been applied to phase analysis of oxygen-containing and silicate ores; chlorite and pseudochlorite[837] minerals can be differentiated. Ilmenite is decomposed in the stream of hydrogen to TiO_2 and metallic iron, which is soluble in diluted HCl.[838] Compounds of zinc, cadmium, and lead can also be reduced to metals; then the elements can be separated from the rock matrix by distillation in a nitrogen stream.[839-841] Hydrogen was employed for chloride separation from synthetic hematite. Produced hydrogen chloride is carried by the gas into a suitable absorber and is determined.[842] Cu-Ni-Fe sulfides, used as collectors for platinum metals, can also be reduced by hydrogen; the platinum metals are determined coulometrically after dissolution in acids.[30,843]

Gaseous halogens, especially chlorine, are the most effective reagents. Chlorine reacts rapidly at an elevated temperature with many metals, yielding corresponding chlorides, differing in their melting and boiling points, on the basis of which they can be separated. Halogenation can also be carried out in aqueous solutions: soluble halides can be separated from insoluble oxides, e.g., SiO_2. In order to prevent changes in solution acidity and consequent changes in the solubilities of the substances present, anhydrous solvents, alcohols, and esters are employed.

Halogenation is carried out by means of halogens alone, by anhydrous hydrogen halides, or by interhalides. Chlorinated hydrocarbon derivatives, such as carbon tetrachloride or chloroform, can also serve as a source of chlorine, as can certain sulfur-containing compounds (e.g., sulfur chloride, sulfuryl chloride, etc.). The apparatus and procedures are very simple and universal: the sample is placed on a boat in the hot zone of the decomposition tube and the reagent gas is passed over it at the given temperature. The tubes are made mainly of fused quartz or suitable ceramics; platinum is satisfactory for gaseous fluorine. Traces of oxygen are removed from the gas by absorption in reducing reagent solutions. The purified gases must be perfectly freed of humidity by drying with desiccating agents, e.g., sulfuric acid, phosphorus pentoxide, or magnesium perchlorate. Devices made of Teflon or other resistant materials were constructed for decompositions in gas streams at low temperatures.[133,321]

Variously volatile chlorides are formed at a slightly increased temperature by the effect of dry chlorine or hydrogen chloride. The chlorides of copper, silver, nickel, cobalt, lead, and some other metals are most stable. Iron and zinc chlorides exhibit medium volatility. Chlorides of sulfur, selenium, tellurium, arsenic, antimony, and tin distill very easily. Among rarer elements, the chlorides of beryllium, zirconium, hafnium, niobium, tantalum, vanadium, molybdenum, tungsten, etc. are volatile. Some platinum metals and their alloys can be decomposed and separated by chlorination. On the other hand, the alkali metals, alkaline earths, and the rare earths are very stable toward chlorine, so that chlorination is advantageously employed for isolation and purification of rare earth element compounds.[844] The selectivity of the distillation separation can be improved by adding graphite or metal oxides to the substance to be decomposed.

The use of halogens for decompositions in inorganic analysis has been reviewed.[270] The applications are usually based on the different behavior of chlorides during heating; molybdenum and vanadium chlorides can thus be separated from tungsten chlorides.[845] Tungsten minerals are decomposed only at high temperatures. Sulfides can readily be decomposed by chlorination; chlorides of sulfur, arsenic, and the other volatile elements mentioned earlier are readily distilled off. The procedure can be advantageously applied to decompositions of sulfosalts and sulfides included in silicate matrix. Rarer germanium compounds, including complicated organo complexes of this element, occurring in coal,[846] are also readily decomposed. Chlorination has attained great importance in the phase study of meteorites. Metallic iron containing nickel, sulfides, and phosphides is decomposed by hydrogen chloride-free chlorine and produced chlorides are distilled off. However, iron oxides and silicates are not attacked. The decomposition of meteorite iron is limited[847,848] by the nickel content (more than 25%) in the alloy. Chlorination is effectively employed for the separation of rare earth element groups from iron and aluminum.[849] A procedure for isolation and purification of rare earth, thorium, and scandium oxides obtained from silicates[249] or radioactive raw materials[844] has been described. Rare earth, niobium, and tantalum minerals, such as fergusonite, samarskite, pyrochlor, and others, are decomposed by chlorination.[844,850] Niobium compounds yield a volatile oxychloride, which is difficult to condense; therefore, it must be reduced to the chloride during the decomposition by adding active charcoal.[851] The varied volatility of aluminum, iron, and zirconium chlorides has been utilized in the determination of the latter in rocks and zirconium concentrates.[852] The same principles underlie technological procedures for the production of this metal with a minimum hafnium content. Transuranium elements up to an atomic number of 98 have been separated on the basis of various volatilities; the distillation is carried out at a programmed temperature.[853] The separation of europium and cerium has also been described.[854]

Chlorination at an elevated temperature is important for the dissolution of metallic gold and platinum metals remaining after fire-assay separation. The platinum metal chlorides have a low volatility, except for osmium and ruthenium chlorides. Chlorination is facilitated by the presence of sodium chloride; while iridium and rhodium yield insoluble compounds in direct chlorination, chlorocomplexes readily soluble in hydrochloric acid are formed in the presence of sodium chloride. This salt also decreases the volatility of platinum and rhodium chlorides.[855] The effect of temperature, the amount of sodium chloride, and chlorination duration on the solubility of the compounds formed was studied.[386] Metal recoveries after chlorination were generally higher than after fire assay and extraction with aqua regia and amounted to 96 to 98% of the initial metal content. Chlorination in a closed system has also been described.[28] Chlorine is also suitable for the decomposition of osmiridium, sperylite, and platinum disulfide.[795] Volatile osmium chloride is absorbed in traps with 6 *N* HCl saturated with a sulfite. Chlorination was also successful in the dissolution of gold grain after cupellation, gold being used as a collector for rhodium.[696] Ore concentrates were analyzed for gold after preliminary reduction with hydrogen, followed by several hours of chlorination at 700°C. Gold was coprecipitated on tellurium[382] from dissolved metal chlorides. In the analysis of native gold, chlorination was employed for the destruction of the residue, after dissolution of the metal in aqua regia. The residue is first extracted by dilute nitric acid, then mixed with sodium chloride and chlorinated.[856]

D. Pyrohydrolysis

Pyrohydrolysis is a special decomposition technique in a gas stream. Materials are decomposed at a high temperature by a stream of water vapors or damp gas in a suitable reaction tube. Volatile acids, especially hydrogen halides and sulfuric, fluorosilicic, and boric acids, are released and can thus be separated from the matrix and determined in the condensate. The decomposition technique was proposed by Warf[857] and has been applied by many authors,[858-877] chiefly for the determination of fluorine. The apparatus and the procedure are practically universal; only the reaction conditions, the temperature, the steam flow rate, the amount of a liquid passed, and the kind of accelerator vary, depending on the composition of the material to be decomposed. Decompositions are carried out in platinum,[857,859-862] nickel,[858,864,865] quartz,[866,867,869-873] glass, and ceramic[868] devices. Some substances, such as fluorides of weakly basic elements, are decomposed very rapidly pyrohydrolytically. On the contrary, alkali metal and alkaline earth fluorides decompose poorly, as the hydrofluoric acid formed reacts again with the strong alkali liberated. These cations must be bound by so-called accelerators, which are thermally stable weakly acidic substances, mostly amphoteric metal oxides, such as uranium(IV)-uranium(VI)[857,862,863,865] oxide, alumina,[859,864] silica,[868,869] vanadium pentoxide,[870,871] and tungsten trioxide.[863,867,868] Overheated water vapor,[857-862,864-866] damp oxygen, or damp air[867-869,871-873] are used for decomposition at temperatures between 800 and 1200°C.

Numerous applications of this method[875-877] have been devoted to the determination of fluorine in rocks and other natural silicates. It has been found that micas with high concentrations of alkali metals are poorly decomposed by the above fusion agents; a 1:1:2 mixture of bismuth(III) oxide, sodium tungstate, and vanadium(V) oxide has proven effective and has been applied to the determination of fluorine in standard rocks.[872] A 1:10 mixture of lithium metaphosphate and U_3O_8 has been recommended for the same purpose.[873] The metaphosphate acts as an efficient acidic fusion agent and excess uranium suppresses the volatility of phosphorus oxides. Sodium or lithium pyrotungstate,[874] acting as a catalyst and a fusion agent, gave good results in the rapid quantitative separation of fluorine from glasses and fluorite.

The other halides[875-879] can be separated under conditions identical to those used for fluorides. The method has been used in the determination of trace amounts of these elements in mineral materials and is especially well suited for geochemical purposes. Final determination of halides can be carried out photometrically or preferably using ion-selective electrodes. Pyrohydrolytic determination of boron has not enjoyed very extensive application because of demanding conditions for the decomposition and incomplete separation of the substance to be determined.

VII. CONCLUSION

The chief methods for the decomposition of natural inorganic compounds have been evaluated. Attention has been centered on a modern, very effective, and promising decomposition technique, namely, decomposition at an elevated temperature and pressure. Further, the decomposing properties of hydrofluoric acid and effective fusion with alkali meta- or tetraborates were dealt with in detail. The latter technique has gained importance with the progress in AAS and other physicochemical methods for the final determination of elements. The introduction of these methods in analytical practice required simple preparation of analytical solutions with a constant background for very heterogeneous materials; therefore, fusion with metaborates has proven most advantageous. Reduction fusion has been broadly discussed in view of the economical importance of the analyzed materials. Other commonly used decomposition techniques employing acids and classical fusion procedures have been evaluated very briefly. Their application is quite general, and no substantial development can be expected using them. In discussing the individual decomposition techniques, their applicability, possibilities of losses in the material, and contamination of the analyzed substances have been stressed.

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