2. PROPERTIES OF ZIRCONIUM

2.1 Physical Properties

Zirconium is the 40th element in the periodic table. It belongs to the titanium subgroup, subgroup IVB, in which hafnium is also placed. Zirconium occurs naturally in the form of five isotopes with mass numbers of 90, 91, 92, 94 and 96 and corresponding natural abundances of 51.46%, 11.23%, 17.11%, 17.40 and 2.80% respectively [13]. A further 26 zirconium radioisotopes occur in the degradation series of other elements [7]. The name zirconium comes from the Persian word *zargun*, which means gold-like metal [7, 18].

Table 2.1: Physical properties of zirconium [12, 14]

Relative atomic mass		91.224
Atomic radius		15.90 nm (in metal lattice)
Ionic radius (Zr^{4+})		7.5 nm
Electronegativity		1.22
Standard potential M/MO_2		1.53 V
Melting point		1 852 ± 2 °C
Boiling point		3850 °C
Density	α -phase	6.50 g/cm^3
	β-phase	6.05 g/cm^3
Specific heat at 25 °C		0.285 $Jg^{-1}kg^{-1}$
Thermal conductivity at 25 °C		21.1 $Wm^{-1}K^{-1}$
Thermal expansion at 25 °C (α)		5.89×10^{-6} K^{-1}
Ionisation potential	1st	674.1 kJ mol^{-1}
	2nd	1 268 kJ mol^{-1}
	3rd	2 217 kJ mol^{-1}
	4th	3 313 kJ mol^{-1}
Effective cross-section for thermal neutrons		$1.9\times10^{-29}m^2$ (0.19 barns)
Thermal conductivity at 25 °C		21.1 $Wm^{-1}K^{-1}$
	at 100 °C	20.4 $Wm^{-1}K^{-1}$
	at 300 °C	18.7 $Wm^{-1}K^{-1}$

Zirconium is a lustrous metal, hard and ductile, with the appearance of stainless steel, in the form of either platelets or flakes. In powder form, the colour is bluish-black. Pure zirconium shows three solid phases. The ω-Zr phase is stable below 200 K, 1 atm and up to 200 K at 6 GPa. The α-Zr phase is stable between 200 K and 1 125 K. The β-phase is stable from 1 125

K up to the melting point [12, 14]. Some important physical properties of zirconium are summarised in Table 2.1.

Zirconium is an elastic metal, like other metals with lower melting points. Its strength diminishes with increasing temperature. The presence of contaminants and a crystalline texture influences its properties. Small amounts of contaminants can drastically reduce its corrosion resistance [12, 13].

2.2 Chemical Properties

Zirconium is able to form compounds with 1, 2, 3 or 4 valences. Oxidation states lower than 4 are difficult to find. Zirconium compounds commonly exhibit coordination numbers of 4, 6, 7 and 8, with tetrahedral, octahedral, pentagonal bipyramidal and dodecahedral forms respectively. Crystalline structures, featuring coordination numbers equal to 7 or 8, with capped trigonal prismatic and square antiprismatic forms respectively, are also known [14, 15, 18].

Considering that in stereochemistry zirconium ions are found to be highly charged, spherical and very large, with no partially filled shells, it is understandable that compounds of zirconium (IV) have high coordination numbers (6, 7 and 8) and a great variety of coordination polyhedra [2, 14]. A further consequence of the high charge-to-radius is that the aqueous solution chemistry is dominated by hydrolysis and the presence of polymeric species. These species are sensitive to their environment and their equilibrium is established slowly, making study results difficult to obtain. The practical effect of this is that it is difficult to control the production of zirconium chemicals with consistent properties [2].

Zirconium forms one stable oxide, with an oxidation number equal to 4 (ZrO_2). Oxygen dissolved in the zirconium metal lattice makes it possible to discover some low oxides, such as $ZrO_{0.3}$. Zirconium monoxide has been detected in some stars by mass spectrographic measurements and it can also be found evaporated on the surface of tungsten filaments [5, 12, 13, 15]. Other oxygen pseudo-compounds can be observed when oxygen is added in the form of alpha zirconium. Those pseudo-compounds represent oxygen dissolution in the zirconium lattice [15]. New research results have indicated that zirconium monoxide is produced by the reduction of zirconium dioxide with magnesium; indeed some studies refer to it as the major phase produced [19]. However, electrochemical studies have questioned the existence of this species, suggesting that zirconium monoxide may be a mixture of zirconium and zirconium dioxide [20].

When a hydroxide solution is added to a solution of zirconium (IV), a white gelatinous precipitate is generated, $ZrO_2.nH_2O$. The water content is variable. The existence of true hydroxides is disputed [14]. Nevertheless, hydrous zirconium dioxide has been accepted as equivalent to zirconium hydroxide. Huang *et al.* [21] have established the differences between hydrous zirconium dioxide and hydrated zirconium hydroxide, $Zr(OH)_4.nH_2O$, on the assumption that zirconium hydroxide does exist. Baddeleyite, zirconia in monoclinic (form, has a structure in which the metal atom exhibits a coordination number equal to 7 [14].

Chemically, zirconium is highly reactive – in air or in aqueous media, it promptly develops an oxide film, which makes it stable with regard to corrosion. The stability can, however, be drastically reduced by fluoride ions, even in trace amounts [12].

Zirconium is stable in both acid and caustic media. At high temperatures it is attacked slowly by aqua regia, phosphoric acid, hydrofluoric acid and sulphuric acid. At high concentrations in acidic media, zirconium may be attacked rapidly. It is also attacked by molten sodium bisulphate, sodium carbonate and sodium peroxide. The formation of a black film protects it against molten sodium hydroxide. Zirconium is totally resistant to corrosion by organic acids [13].

Compounds in which zirconium forms an oxy-anion are called zirconates. These compounds can be obtained by combining oxides, hydroxides and nitrates of other metals with similar zirconium compounds and firing the mixtures at 1 000 to 2 500 °C. The salts are, in fact, mixtures of metal oxides. Discrete zirconate ions are not known [14].

With zirconium, the other elements of the oxygen group form compounds similar to zirconia, ZrY_2, where Y can be sulphur, selenium or tellurium. Those compounds are semiconductors [14].

Zirconium metal reacts with CO_2, CO, SO_2, steam, nitrogen and nitrogen oxides more slowly than with air. At higher temperatures, zirconium reacts with hydrogen, oxygen, nitrogen and halogens. The reaction with hydrogen is reversible. When finely divided, it is pyrophoric. Zirconium powder reacts with many other elements, such as hydrogen, boron, carbon, nitrogen and the halogens. The ignition temperature for the process is above 200 °C. The reaction of platinum and zirconium powder is violent [12, 13, 15].

Zirconium forms alloys with various metals. It can also be added in small amounts to other metals to enhance their properties [12, 13].

In aqueous media, zirconium ions tend strongly to hydrolyse. This is attributed to the high charge of the ions. Free ions exist at very low concentrations ($\approx 10^{-4}$ M) and high acidity (1-2 M of $[H^+]$) [14]. The stability of zirconium in the electrochemical series lies below that of water, suggesting that zirconium will decompose in water through the evolution of hydrogen, dissolving as zirconic ions (Zr^{4+}) and zirconyl ions (ZrO^{2+}) in very acid solutions, and as zirconate ions ($HZrO_3^-$) in very alkaline solutions. In moderately acid, neutral and moderately alkaline solutions, the metal will be covered with a thin film of oxide [20].

Because of the low value of the reduction potential of zirconic, zirconyl and zirconate ions with respect to metallic zirconium, the electrolytic separation of zirconium from aqueous solutions is not practicable. Molten salts (potassium zirconifluoride or a mixture of zirconium and sodium chlorides) can be electrolysed to give an impure powdery metal. Zirconium can be displaced by zinc in solutions of anhydrous zirconium sulphate in methyl alcohol [20].

Zirconium forms basic salts with sulphates and chromates. These salts contain infinite chains of composition $[M(\mu\text{-}OH)_2]_n^{2n+}$. The coordination number of the metal in those complexes rises to 7 and 8 [14].

Zirconium can exhibit other oxidation states, but no free ions are known to exist in those states. For oxidation state III, trihalides are known, namely $ZrCl_3$, $ZrBr_3$ and ZrI_3. There are several methods of synthesis. One of them involves the reduction of ZrX_4 in molten AlX_3, with aluminium or zirconium. Zirconium halides are reduced faster than hafnium halides. This process can therefore be used to separate zirconium from hafnium contaminants. [14].

Lower oxidation states than III do exist. Compounds such as ZrCl and ZrBr are obtained by reaction of ZrX_4 with zirconium metal at 800 to 850 °C. These compounds have high thermal stability, with a melting point above 1 100 °C. They have a metallic character and cleave like graphite. Both compounds may incorporate oxygen or hydrogen [14]. Halides of zirconium (II) and zirconium monoxide are also known [14]. Halides can be made through the reduction of ZrX_4 (where X can be chlorine, bromine or iodine) with zirconium metal in sealed tantalum containers [14].

2.3 Toxicity of Zirconium

Zirconium seems to be non-toxic as an element and in its compound forms. Physiologically, the pH of zirconium is associated with biological activity, but it is inert in human tissue. For this reason, some of its compounds have been used in the cosmetics industry. Zirconium applied in antiperspirants has been found to be a probable cause of skin and lung granulomas [12].

Strongly acidic compounds of zirconium, such as zirconium tetrabromide, tetrachloride, tetrafluoride, tetraiodide, tetranitrate and sulphate, are strongly corrosive to the eyes, lungs, skin, mouth, oesophagus and stomach. That is due to the compound's acidic nature, which can lead to hydrolysis in contact with animal and plant tissue [12].

The oral toxicity is very low, the maximum for pulmonary exposure being at a level of 5 mg of zirconium per m^3 [15].

Although metallic zirconium is non-toxic, finely divided zirconium metal (powder, dust, chips, foil, sponge) must be handled with care because it is easily ignitable in air. Workers dealing with zirconium chips or other forms of finely divided zirconium should wear heat-reflectant clothing [12].

A zirconium fire can only be extinguished by disrupting the oxygen supply. Other oxidants, such as water, carbon dioxide, carbon tetrachloride, iron oxide and limestone, must be removed to control a zirconium fire. Small fires can be smothered by dousing with dry silica sand or dry table salt, or by using argon or helium if the zirconium is in a closed container. Large-scale fires are allowed to burn out, while protecting the surroundings from ignition. The use of water is strictly prohibited in zirconium fires [12].

Finely divided zirconium metal is classified as a flammable solid and specific regulations are prescribed for its transportation [15].

Solutions that corrode zirconium metal react violently or explosively with finely divided zirconium [12]. In terms of sensitivity, zirconium is an eye irritant [7].

2.4 Industrial Importance of Zirconium Chemicals

2.4.1 Zirconium basic sulphate

This is a key product in the production of pure zirconium chemicals because it is possible to control the form in which it is precipitated. It can be obtained by reducing the acidity of zirconium sulphate solution. The basis of the formation of zirconium basic sulphate is related to the fact that the dissolution of zirconium sulphate sheets occurs by breaking the bonds between sulphate groups and zirconium atoms, via replacement of the sulphate groups with hydroxy groups as ligands. The structure is composed of single strands of $[Zr(OH)_2]_n^{2n+}$, joined by bridging sulphates [2, 16].

In this compound, zirconium atoms predominantly have a coordination number of 8. The most common zirconium basic sulphate is $Zr_5O_7(SO_4)_3.nH_2O$. Other basic sulphates have been formulated in the literature. The dodecahedral structure consists of layers of ZrO_8 bridged by sulphate ions. Another zirconium basic sulphate, $Zr(OH)_2SO_4$, has a square antiprism and is composed of infinite zigzag chains of $[Zr(OH)_2]$ [12, 13].

Sulphate ions have a strong affinity for zirconium and therefore other sulphate salts of zirconium are known, as well as various anionic sulphato-complexes in solutions. These salts are referred to as normal salts to distinguish them from the basic and acid salts. The key to this definition lies in the SO_4/Zr ratio. If this ratio is equal to 2, the salt is defined as neutral or normal, although these salts exhibit a strongly acidic behaviour. If the ratio is less than 2, then the salt is referred to as basic (in contrast to acid); these salts are also called anionic salts [12, 13, 16, 22].

Zirconium orthosulphate solutions are highly acidic. They can be made from zirconium basic sulphate or carbonate, or by the direct dissolution of baddeleyite in sulphuric acid. The salt crystallises directly from the solution in the form of a tetrahydrate, $Zr(SO_4)_2.4H_2O$. By heating it at 100 °C, the tetrahydrate can be converted to a monohydrate and from a monohydrate it becomes anhydrous at 380 °C [2, 12, 13, 22]. Higher hydrates are also known [13].

Zirconium basic sulphate is used in the production of zirconium basic carbonate and zirconium hydroxide, and therefore to produce zirconia via zirconium hydroxide. It is also used to produce the so-called zirconium soaps, which are paint driers. Fresh zirconium sulphate solutions are preferred for use in leather tanning over chromium solutions. Mixtures of sulphate solutions of chromium, zirconium and aluminium have been proposed. Zirconium sulphate is used in photography, as a pigment coating and in the treatment of wool-fabric to confer flame resistance. Zirconium sulphate is also used in the catalysis of many reactions related to hydrocarbon processing in oil refineries, where it is referred to as a most active catalyst [2, 12, 15, 16, 23].

2.4.2 Zirconium carbonate

From the theoretical point of view, there are two kinds of carbonate salts of zirconium: the normal and the basic salts. In practice, only basic salts are known [13]. Nominally, basic zirconium carbonate is $2ZrO_2.CO_2.xH_2O$. The ratio of ZrO_2 to CO_2 may range from 4:1 to 1:1 [15].

It is produced in a two-step process. First, zirconium sulphate is produced from an oxychloride salt solution. The carbonate is formed through an exchange reaction between the water slurry of zirconium basic sulphate and sodium carbonate or ammonium carbonate at 80 °C, under controlled pH conditions [15, 16].

Freshly produced zirconium hydroxide dispersed in water can easily absorb carbon dioxide to form zirconium basic carbonate. Once washed free of other anions, it can be dissolved in organic acids such as acetic to form the corresponding oxysalts [15].

Ammonium zirconium carbonate enhances the fungicidal action of copper salts on cotton cloth, and zirconium acetate has been used as an algaecide. Both zirconium carbonate and zirconium oxyacetate have been used in the waterproofing of fabrics. Zirconium carbonate is also used in floor polishes [15].

2.4.3 Zirconium chlorides

Zirconium oxide dichloride, $ZrOCl_2.8H_2O$, commonly called zirconium oxychloride, is really a hydroxyl chloride, $[Zr_4(OH)_8.16H_2O]Cl_8.12H_2O$. It is commercially produced by the caustic fusion of zircon. The cake is then washed with water. Sodium zirconate hydrolyses to hydrous zirconia, which is reacted with hot hydrochloric acid. Zirconium oxychloride is recovered by crystallisation. Zirconium oxychloride can also be produced by the dissolution of zirconium tetrachloride in water, or by reacting zirconium carbonate with hydrochloric acid [2, 12, 15, 16, 24].

Zirconium oxychloride is an important basic material in the production of other zirconium chemicals. The salt cannot be dried to the anhydrous form; it decomposes to hydrogen chloride and zirconium oxide. Anhydrous zirconium oxychloride is produced by reaction of dichlorine oxide (phosgene) with a zirconium tetrachloride suspension in carbon tetrachloride. The reaction starts at –30 °C. The compound is solid and extremely hygroscopic; it decomposes to zirconia and zirconium tetrachloride at 250 °C [15].

Zirconium tetrachloride is produced by zirconia carbochlorination, or by reacting zirconium metal with chlorine, hydrogen chloride or phosgene. Chlorinated hydrocarbons, particularly carbon tetrachloride, chloroform or hexachloroethane, can be used as chlorinating agents on a laboratory scale. Zirconium tetrachloride is also formed by reacting ferrozirconium or silicozirconium with iron (II) chloride at elevated temperatures [12, 15].

Zirconium tetrachloride reacts rapidly with water, vapour or liquid to exchange two chlorines for oxygen. In powder form, it reacts in water to form zirconium hydroxychloride and free hydrochloric acid [12, 15].

Zirconium tetrachloride is used to produce zirconium organometallic compounds, e.g. reacted with alcohols to form alkoxides, to form zirconium nitride coatings, and electrochemically transformed into zirconia at high temperatures in fuel cells [2, 12].

Zirconium hydroxychloride and oxychloride are used in the oil industry to stabilise the oil viscosity, and as a clay stabiliser, in wool flameproofing, and in antiperspirants [2].

2.4.4 Zirconium fluorides

Mixing hydrogen fluoride and zirconium tetrachloride at 350 °C produces anhydrous zirconium tetrafluoride, ZrF_4. The zirconium produced in this way has high purity. Hydrofluorination of zirconia at 25 °C, followed by a purifying sublimation in hydrogen fluoride at 825 °C, is another method of processing zirconium tetrafluoride. Direct fluorination of the metal is not indicated due to the low volatility of zirconium tetrafluoride, which coats the surface of the metal. The reaction has to be done at 800 °C to avoid coating the surface [12, 15].

Anhydrous zirconium tetrafluoride with very high purity is a major constituent of some fluoride glasses. These glasses have been specially developed because of their transparency in the near-UV (ultraviolet) to mid-IR (infrared), 0.3-6 μm range. The glasses are held to be better than those of quartz optical fibre. Potassium hexafluorozirconate is used to introduce zirconium into molten aluminium and magnesium as a grain refiner. It is also used in wool flameproofing and in metal conversion coatings [2, 12, 15].

2.4.5 Zirconium phosphates

All phosphates of the titanium group precipitate in strongly acidic solutions. This is important in the analytical separation of zirconium from other elements and in preparing zirconium phosphate. The salt precipitates in gelatinous amorphous form, with variable composition. If the precipitate is refluxed in strong phosphoric acid, a crystalline and stoichiometrically constant compound, $Zr(HPO_4)_2.H_2O$, is obtained. Zirconium bis (monohydrogen phosphate) can also be obtained by gradual precipitation of the phosphate from heated zirconium fluoride solution [13, 15]. Zirconium phosphate hydrolyses in strong basic media to give hydrous zirconia [15].

Zirconium phosphate absorbs caesium and other radioactive-decay products. For this reason, it has been proposed for use as part of permanent disposal systems for nuclear fuel waste processing. Sodium hydrogen zirconium phosphate is used in portable kidney dialysis systems to regenerate and recirculate the dialysate solution. The solution picks up urea during the dialysis. Urea reacts with urease to form ammonia, which is absorbed by sodium hydrogen zirconium phosphate [2, 13, 15]. Zirconium phosphate can act as an intercalation compound because of its structure and bonding between the layers [12].

2.4.6 Zirconium hydride

Zirconium hydride, ZrH_2, is prepared by the reversible absorption of hydrogen on a heated zirconium surface (sponge or ingots). The metal is heated above 600 °C in an inert atmosphere or a vacuum to remove the surface oxide film [12].

Zirconia can also be reduced by calcium hydride to form zirconium hydride. This method produces a fine powder (2 - 5 μm) for use in pyrotechnics, such as fuses or fireworks [12].

Zirconium hydride is not a true compound with a fixed stoichiometry, but a series of crystalline phases in which zirconium metal transforms with changing hydrogen concentration and temperature. Most commercial zirconium hydride powder contains 60 - 64% and more of hydrogen [12, 15].

Zirconium hydride has been used in the nuclear industry as a moderator for thermal neutrons in compact, high-temperature reactors. It is also of interest for hydrogen storage and nickel-based hydrogen battery applications [12].

2.4.7 Zirconium nitrides

Zirconium nitride, ZrN, is a gold-coloured, hard, brittle metallic nitride. It is thermally and chemically stable, and has low resistivity. It is an interstitial compound with a NaCl-type cubic structure [12, 15].

Zirconium nitride is prepared by heating zirconium loose sponge or zirconium hydride to 1 100 – 1 500 °C in a nitrogen or ammonia atmosphere. The reaction rate is limited by the slow rate of nitrogen diffusion into the nitride protective layer. Stoichiometric nitrogen amounts require time and high temperatures [12, 15].

Zirconium nitride has been used as a wear-resistant coating on steel drills and cemented-carbide tool bits, as a decorative coating, as a protective coating on steel vessels handling molten metal, and as a surface film on solar energy collectors [12]. In some of these applications, it is being replaced by its analogues titanium nitride, and hafnium nitride [15].

2.4.8 Zirconium carbide

Zirconium carbide, ZrC, is a hard dark-grey brittle solid. It is an interstitial carbide with carbon atoms occupying the octahedral interstices of the zirconium lattice. It is made by the carbothermic reduction of zirconia in an induction-heated vacuum or a hydrogen atmosphere furnace at 1 600 °C. The zirconium carbide produced in this way is porous and light. Milling it and refiring it above 2 200°C produces a dense powder. It can also be produced from zircon by reduction with coke in an electric arc furnace. Heating zirconium tetrachloride with methane in a hydrogen atmosphere at 1 200°C deposits zirconium carbide. Pure zirconium metal and fine graphite powder react exothermically to form zirconium carbide; the reaction needs to be initiated [12, 15].

Zirconium carbide is inert to various reagents. It is dissolved by hydrofluoric acid solutions that also contain nitrate or peroxide ions, and by hot sulphuric acid. It reacts with halogens above 250 °C to form zirconium tetrahalides. It oxidises to zirconium dioxide in air at above 700 °C. Zirconium carbide is an electrical conductor and does not hydrolyse in water. It melts at 3 420 °C [13, 15].

Because it is hard, with a high melting point, zirconium carbide has been under consideration as a constituent of uranium carbide fuelled reactors. It is also used in tool bits in thin film form [13, 15].

2.4.9 Zirconium borides

Three borides of zirconium are known from the zirconium-boron system, namely zirconium monoboride, ZrB, zirconium diboride, ZrB_2, and zirconium dodecaboride, ZrB_{12}. Zirconium diboride is the only one that is chemically and thermally stable. It is a grey refractory solid with a hexagonal crystal structure and melts at 3 245 °C. It is considered to have the best oxidation resistance of all refractory hard metals. Zirconium diboride also has excellent thermal shock resistance [12, 15].

Technical-grade zirconium diboride can be produced by reacting zircon, boron oxide and carbon in a submerged-electrode arc furnace. The pure compound is produced by co-reduction of zirconium tetrachloride and boron trichloride with hydrogen or aluminium in a chloride bath. Another process consists of a carbothermic reduction of zirconia and boron carbide. The use of boron oxide in this process is not appropriate because of its relatively high vapour pressure under working conditions (1 400 °C) [12, 15]. In the film form, it is produced by subliming zirconium tetrahydridoborate at 25 °C in a vacuum and passing the vapour over the substrate heated to 250 °C [12].

Zirconium tetrahydridoborate, $Zr(BH_4)_4$, is prepared by the reaction of zirconium tetrachloride with lithium tetrahydridoborate in diethyl ether, followed by double distillation at 20 °C. It has a tetrahedral structure, with three hydrogen atoms bridging the zirconium atom and each boron atom [12].

Zirconium tetrahydridoborate is one of the most volatile zirconium compounds: it melts at 29 °C and boils at 118 °C. Its vapour pressure at 25 °C is 2 kPa. It decomposes near 250 °C, forming zirconium boride and it ignites in contact with dry air [12].

Zirconium diboride is used as a diffusion barrier in semiconductors, as a container for molten metals, and as a burnable absorber in nuclear reactor cores. Zirconium tetrahydridoborate catalyses the polymerisation of unsaturated hydrocarbons, and reacts with aliphatic alcohols to form zirconium and boron alkoxides [12].

2.5 Analytical Aspects of Zirconium

Zirconium is qualitatively determined by a "spot test" using *p*-dimethylamino-azophenylarsonic acid in hydrochloric acid (1-2N) in the presence of hydrogen peroxide. It gives a brown precipitate. For differentiation between hafnium and zirconium, rufigallic acid in hydrochloric acid solution is used. Zirconium produces a deep purple colour, while hafnium has a light pink precipitate [13].

The most common quantitative method for determining zirconium is a gravimetric method involving ignition to zirconia after precipitation with mandelic acid, or ignition to ZrP_2O_7 after precipitation with phosphate ions. However, these precipitants are not specific for zirconium, leading to a determination of zirconium plus hafnium. There are a number of inorganic (approximately 10) and organic (around 42) precipitants that can be used in the gravimetric determination of zirconium [12, 15].

Volumetrically, zirconium is determined by a complexometric method using EDTA at pH 2.0, back-titrating with bismuth (III) and thiourea as indicator [13, 15]. In air samples, plasma emission spectroscopy is used [12].

Colorimetric methods are used to determine zirconium plus hafnium. Commonly, these methods include a separation step, such as solvent extraction. Three reagents are employed, namely 8-hydroxyquinoline, alizarin red S and catechol violet [15].

For the determination of hafnium in zirconium atomic absorption spectroscopy, mass spectrography, X-ray fluorescence spectroscopy and neutron activation methods can be used [12].

Impurities in zirconium and zirconium compounds are determined by emission spectroscopy, with arc-spark or plasma excitation. Atomic absorption spectroscopy can also be used. Sulphur and carbon in zirconium are measured by combustion, followed by chromatographic or infrared determination of the oxides. Hydrogen is determined by thermal conductivity after hot vacuum extraction, or by fusion of zirconium with a transition metal in an inert atmosphere and subsequent separation by gas chromatography. For oxygen and nitrogen, the fusion is carried out in the presence of carbon. Phosphorus is determined by visible spectroscopy using molybdenum blue. The more rapid method includes phosphine evaluation or a flame emission technique. Chlorine in low levels is determined by silver precipitation and silver by X-ray or atomic absorption spectroscopy. High levels of chlorine and fluorides are determined by using selective ion electrodes [12].