PERCHLORIC ACID AND PERCHLORATES

1. Introduction

Perchloric acid [7601-90-3], $HClO_4$, is one of the strongest of the mineral acids. The perchlorates are more stable than the other chlorine oxyanions, ie, chlorates, $ClO^-{}_3$; chlorites, $ClO^-{}_2$; or hypochlorites, OCl^- (3) (see DICHLORINE MONOXIDE, HYPOCHLOROUS ACID, AND HYPOCHLORITES). Essentially, all of the commercial perchlorate compounds are prepared either directly or indirectly by electrochemical oxidation of chlorine compounds (4–8) (see CHLORINE; ELECTROCHEMICAL PROCESSING, INTRODUCTION). The perchlorates of practically all the electropositive metals are known, except for a few cations having low charges.

The most outstanding property of the perchlorates is their oxidizing ability. On heating, these compounds decompose into chlorine, chlorides, and oxygen gas. Aqueous perchlorate solutions exhibit little or no oxidizing power when dilute or cold. However, hot concentrated perchloric acid is a powerful oxidizer and whenever it contacts oxidizable matter extreme caution is required. The acidified concentrated solutions of perchlorate salts must also be handled with caution. Ammonium perchlorate [7790-98-9] (AP) is one of the most important perchlorates owing to its high (54.5%) O_2 content and the absence of residue on decomposition. These properties, along with a long shelf life, make it a useful rocket propellant (see EXPLOSIVES AND PROPELLANTS) (9). AP is a true explosive as demonstrated by the explosion at the PEPCON plant at Henderson, Nevada, in 1988 (10).

Following early (1890s) work (11), France, Germany, Switzerland, and the United States began to produce perchlorates for use as propellants and explosives. Whereas total world production of perchlorates did not exceed 1800 t/yr until 1940, it increased dramatically during World War II to about 18,000 t/yr in order to supply the rocket and missile industries. Actual perchlorate production is difficult to determine in any given year, because AP is classified as a strategic material. Future production is expected to depend mostly on space programs.

2. Properties

2.1. Chlorine Heptoxide.

The anhydride of perchloric acid is chlorine heptoxide [10294-48-1], Cl_2O_7, also known as dichlorine heptoxide. It is obtained as a colorless oily liquid by dehydration of perchloric acid using a strong dehydrating agent such as phosphorus pentoxide, P_2O_5 (12,13):

$$2\,HClO_4 + P_2O_5 \longrightarrow Cl_2O_7 + 2\,HPO_3 \qquad (1)$$

The Cl_2O_7 decomposes spontaneously on standing for a few days. The acid dehydration reaction requires a day for completion at $-10°C$ and explosions can occur. Upon ozonation of chlorine or gaseous ClO_2 at 30°C, Cl_2O_7 is formed (13).

Chlorine heptoxide is more stable than either chlorine monoxide or chlorine dioxide; however, the Cl_2O_7 detonates when heated or subjected to shock. It melts at −91.5°C, boils at 80°C, has a molecular weight of 182.914, a heat of vaporization of 34.7 kJ/mol (8.29 kcal/mol), and, at 0°C, a vapor pressure of 3.2 kPa (23.7 mm Hg) and a density of 1.86 g/mL (14,15). The infrared spectrum is consistent with the structure $O_3ClOClO_3$ (16). Cl_2O_7 decomposes to chlorine and oxygen at low (0.2–10.7 kPa (1.5–80 mm Hg)) pressures and in a temperature range of 100–120°C (17). It is soluble in benzene, slowly attacking the solvent with water to form perchloric acid; it also reacts with iodine to form iodine pentoxide and explodes on contact with a flame or by percussion. Reaction with olefins yields the impact-sensitive alkyl perchlorates (18).

2.2. Perchloric Acid. Pure anhydrous perchloric acid, $HClO_4$, is quite unstable. In aqueous solution, however, $HClO_4$ is a familiar and useful reagent. The acid is the strongest simple acid and the perchlorate ion the least polarizable negative ion known. Perchloric acid is commonly obtained as an aqueous solution, although the pure anhydrous compound can be prepared by vacuum distillation as a colorless liquid, which freezes at −112°C and boils at 16°C at 2.4 kPa (18 mm Hg) without decomposition. The pure acid cannot be distilled at ordinary pressures and explodes at 90°C after standing at room temperature for 10–30 days. The aqueous solution can be concentrated by boiling at 101 kPa (1 atm) at 203°C, at which point an azeotropic solution is attained which contains 72.4% $HClO_4$. For purification by distillation, reduced pressure is needed below 200 mm to avoid partial decomposition to chlorine, chlorine oxides, and oxygen (19–24).

A number of hydrates of perchloric acid, $HClO_4 \cdot nH_2O$, where $n = 1, 2, 2.5, 3$, and 3.5, are known. These are commonly referred to as the hydronium or oxonium perchlorates, $H_3O^+ClO^-{}_4$, because of the analogy between the x-ray patterns of these species and ammonium perchlorate. Commercial 72% perchloric acid contains only slightly more water than the dihydrate (25). When cold or dilute, perchloric acid is a weak oxidizing agent. When hot and concentrated, however, its oxidizing power increases to the point that it can act explosively in the presence of a reducing agent (26).

The combination of oxidizing effect, acidic strength, and high solubility of salts makes perchloric acid a valuable analytical reagent. It is often employed in studies where the absence of complex ions must be ensured. The value of wet ashing techniques, in which perchloric acid is used to destroy organics prior to elemental analysis for the determination of trace metals in organics, has been well established (see TRACE AND RESIDUE ANALYSIS).

Perchloric acid can be prepared by the treatment of perchlorates with sulfuric acid followed by distillation. A modification of the procedure (21) involves the reaction of ammonium perchlorate with nitric and hydrochloric acids, and then concentration at 198–200°C to eliminate the unreacted acids by vacuum distillation:

$$34\ NH_4ClO_4 + 36\ HNO_3 + 8\ HCl \longrightarrow 34\ HClO_4 + 4\ Cl_2 + 35\ N_2O + 73\ H_2O \quad (2)$$

The electrolytic oxidation of chlorate to perchloric acid is also feasible (27). Perchlorates are commonly prepared by electrolytic oxidation of chlorates:

$$H_2O \longrightarrow O^{\cdot} + 2\,H^+ + 2\,e^- \tag{3}$$

$$HClO_3 + O^{\cdot} \longrightarrow HClO_4 \tag{4}$$

Electrochemical perchloric acid formation begins at 2.4 volts and reaches a maximum at 2.8–2.9 volts; lowering the temperature to −20°C can accelerate the process significantly (28).

When solid potassium chlorate is carefully heated, it can be transformed into perchlorate thermally:

$$4\,KClO_3 \longrightarrow 3\,KClO_4 + KCl \tag{5}$$

2.3. Ammonium Perchlorate. Heats of formation for the metal perchlorates are nearly the same as those for the corresponding chlorides, so that the reaction

$$MClO_4 \longrightarrow MCl + 2\,O_2 \tag{6}$$

takes place with little net energy change. It is for this reason that the perchlorates, especially those of the light metals and ammonium ion, are favored as solid oxidizers for rocket propellants.

Ammonium perchlorate is a colorless, crystalline compound having a density of 1.95 g/mL and a molecular weight of 117.5. It is prepared by a double displacement reaction between sodium perchlorate and ammonium chloride, and is crystallized from water as the anhydrous salt.

Because of the use of ammonium perchlorate as a solid oxidizer for rocket propellants, the thermal decomposition has been much studied (29–32). Three separate activation energies have been observed for AP decompositions: an activation energy of 123.8 kJ/mol (29.6 kcal/mol) is found below 240°C; of 79.1 kJ/mol (18.9 kcal/mol) above 240°C; and finally, of 307.1 kJ/mol (73.4 kcal/mol) between 400–440°C (33,34). Below 300°C, the equation

$$4\,NH_4ClO_4 \longrightarrow 2\,Cl_2 + 3\,O_2 + 8\,H_2O + 2\,N_2O \tag{7}$$

represents the primary products. Above 300°C, the proportion of nitric oxide increases; and above 350°C, the gas analysis suggests the following (32):

$$\begin{aligned} 10\,NH_4ClO_4 \longrightarrow {} & 2.5\,Cl_2 + 2.5\,NOCl + HClO_4 + 1.5\,HCl + 18.75\,H_2O + 1.75\,N_2 \\ & + 6.375\,O_2 + 2\,N_2O \end{aligned} \tag{8}$$

In commercial manufacture of ammonium perchlorate, sodium perchlorate can be the starting material. The ammonium ion can be contributed by such materials as ammonium chloride, sulfate, and nitrate, eg, the metathetical reaction of sodium perchlorate and ammonium chloride:

$$NaClO_4 + NH_4Cl \longrightarrow NH_4ClO_4 + NaCl \tag{9}$$

In a modification of equation 9 (35),

$$NH_3 + HCl + NaClO_4 \longrightarrow NH_4ClO_4 + NaCl \qquad (10)$$

A newer approach developed for producing commercial quantities of high purity AP (8,36) involves the electrolytic conversion of chloric acid [7790-93-4] to perchloric acid, which is neutralized by using ammonia gas:

$$HClO_3 + H_2O \longrightarrow HClO_4 + H_2 \qquad (11)$$

$$HClO_4 + NH_3 \longrightarrow NH_4ClO_4 \qquad (12)$$

The ammonium perchlorate solution is spray-dried to the desired crystal size at air temperatures below 150°C and crystal temperatures of about 110°C. This procedure provides a pure product having a controlled grain size. Prior mechanical and thermal treatment affects the isothermal decomposition of AP at 215–235°C (37).

2.4. Alkali Metal Perchlorates. The anhydrous salts of the Group 1 (IA) or alkali metal perchlorates are isomorphous with one another as well as with ammonium perchlorate. Crystal structures have been determined by optical and x-ray methods (38). With the exception of lithium perchlorate, the compounds all exhibit dimorphism when undergoing transitions from rhombic to cubic forms at characteristic temperatures (33,34). Potassium perchlorate [7778-74-7], $KClO_4$, the first such compound discovered, is used in pyrotechnics (qv) and has the highest percentage of oxygen (60.1%).

The alkali metal perchlorates are either white or colorless, and have increasing solubility in water in the order of $Na > Li > NH_4 > K > Rb > Cs$. The high solubility of sodium perchlorate, $NaClO_4$, makes this material useful as an intermediate for production of all other perchlorates by double metathesis reactions and controlled crystallization.

2.5. Group 11 (IB) Perchlorates. Copper and silver perchlorates have been studied quite extensively. Copper(I) perchlorate [17031-33-3], $CuClO_4$, and copper(II) perchlorate [13770-18-8], $Cu(ClO_4)_2$, form a number of complexes with ammonia, pyridine, and organic derivatives of these compounds. The copper perchlorate is an effective burn-rate accelerator for solid propellants (39).

The silver perchlorate [7783-93-9] salt, $AgClO_4$, is deliquescent and forms a light-sensitive monohydrate that can be dehydrated at 43°C and is soluble in a variety of organic solvents. Explosions of silver perchlorate have been reported (40–42). Gold forms organic perchlorate [42774-61-8] complexes as well as complexes with silver, eg, $(C_6H_5)_3AgAu(C_6F_5)_2ClO_4$.

2.6. Alkaline-Earth Perchlorates. Anhydrous alkaline-earth metal perchlorates can be prepared by heating ammonium perchlorate in the presence of the corresponding oxides or carbonates (43). The hydrates can be prepared by treatment of the metal oxides or various salts with aqueous perchloric acid (44). The alkaline-earth perchlorates are unusually soluble in organic solvents (44). The basic salts $M(OH)ClO_4$, where M is Mg, Ca, or Ba, have also been prepared and characterized (45). Beryllium perchlorate [39455-86-2], $Be_4O(ClO_4)_6$, has been prepared by allowing the $BeCl_2$ salt and $HClO_4$ to react or by heating $BeCl_2$ and $HClO_4{\cdot}H_2O$ at 60°C (46). The dihydrate forms.

2.7. Group 12 (IIB) Perchlorates. The zinc perchlorate [13637-61-1], cadmium perchlorate [13760-37-7], mercury(I) perchlorate [13932-02-0], and mercury(II) perchlorate [7616-83-3] all exist. Cell potential measurements show that zinc and cadmium perchlorates are completely dissociated in concentrations up to 0.1 molar in aqueous solutions (47–49). Mercurous perchlorate forms a tetrahydrate that can be readily converted to the dihydrate on heating to above 36°C (50).

2.8. Group 13 (IIIA) Perchlorates. Perchlorate compounds of boron and aluminum are known. Boron perchlorates occur as double salts with alkali metal perchlorates, eg, cesium boron tetraperchlorate [33152-95-3], $Cs(B(ClO_4)_4)$ (51). Aluminum perchlorate [14452-95-3], $Al(ClO_4)_3$, forms a series of hydrates having 3, 6, 9, or 15 moles of water per mole of compound. The anhydrous salt is prepared from the trihydrate by drying under reduced pressure at 145–155°C over P_2O_5 (52).

2.9. Group 3 (IIIB) and Inner Transition-Metal Perchlorates. The rare-earth metal perchlorates of yttrium and lanthanum have been reported (53). Tetravalent cerium perchlorate [14338-93-3], $Ce(ClO_4)_4$, and uranium perchlorate have also been identified (54).

2.10. Group 14 (IVA) Perchlorates. Perchlorates containing organic carbon have been reported, as have diazonium perchlorates, oxonium perchlorates, and the perchlorate esters (55–57). Extreme caution must be used in working with organic perchlorates; many decompose violently when heated, contacted with other reagents, or subjected to mechanical shock. The diazonium perchlorate of *p*-phenylenediamine, $ClO_4N_2(C_6H_4)N_2ClO_4$, was reported in 1910 to be the most explosive substance known (58).

2.11. Group 4 (IVB) Perchlorates. Titanium tetraperchlorate [13498-15-2] sublimes at 70°C, decomposes on aging in a vacuum, and explodes when heated at atmospheric pressure to 130°C (59).

2.12. Group 15 (VA) Perchlorates. Nitrogen perchlorates have been used as oxidizers in rocket propellants. Hydrazine perchlorate [13762-80-6], $NH_2NH_3ClO_4$, and hydrazine diperchlorate, $ClO_4NH_3NH_3ClO_4$, have been investigated as oxidizers for propellant systems (60). Anhydrous salts can be recrystallized from ethanol, where the monoperchlorate adduct melts at 137–138°C and begins to decompose at 145°C. Deflagration results with rapid heating; violent detonation occurs with mechanical impact, shock, or friction.

Nitronium perchlorate, NO_2ClO_4, also called nitryl or nitroxyl perchlorate, is prepared by reaction of dinitrogen pentoxide and anhydrous perchloric acid. This nitrogen-containing perchlorate reacts vigorously with many organic compounds, explosively with some (61). Nitrosyl perchlorate [15605-28-4], $NOClO_4$, is found from Raman spectroscopy to be composed of NO^+ and $ClO_4{}^-$ ions in an orthorhombic crystal structure of density 2.169 g/mL (62–64). Reaction with water produces nitrogen oxides; reaction with methanol, nitromethane. The $NOClO_4$ is made by passing nitric oxide and nitrogen dioxide in 72% perchloric acid. The anhydrous salt is obtained by partially drying the hydrate over P_2O_5 in an atmosphere of nitrogen oxides followed by desiccation in vacuum. Decomposition occurs at 100°C according to the following reaction:

$$2\ NOClO_4 \longrightarrow 2\ ClO_2 + N_2O_5 + 0.5\ O_2 \tag{13}$$

Phosphonium perchlorate, $P(OH)_4ClO_4$, can be formed as a crystalline product that melts at 46–47°C. This compound is obtained by mixing phosphoric and perchloric acids (65).

2.13. Group 5 (VB) Perchlorates. Vanadyl perchlorate [67632-69-3], $VO(ClO_4)_3$, has been prepared in the cold (−45 to 20°C) by the following reaction (66):

$$VOCl_3 + 3\ Cl_2O_4 \longrightarrow VO(ClO_4)_3 + 3\ Cl_2 \tag{14}$$

2.14. Group 16 (VIA) Perchlorates. A perchlorate compound perchloryl sulfate [43059-05-8], $SO_4(ClO_4)_2$ was produced by the low temperature electrolysis of a 12-*N* H_2SO_4 and 3-*N* $HClO_4$ solution. This compound is a strong oxidizer; reaction with toluene, acetone, benzene, or alcohol at room temperature produces an exothermic and explosive reaction. The $SO_4(ClO_4)_2$ is soluble in Freon and CCl_4 without reaction (67).

2.15. Group 6 (VIB) Perchlorates. Both divalent and trivalent chromium perchlorate compounds [13931-95-8; 13527-21-9] have been reported. Anhydrous chromyl perchlorate [60499-74-3] has been prepared in the cold:

$$CrO_2Cl_2 + 2\ Cl_2O_4 \longrightarrow 2\ Cl_2 + CrO_2(ClO_4)_2 \tag{15}$$

Chromyl perchlorate has been suggested for a gas-generating system operating at −45°C (66).

2.16. Group 17 (VIIA) Perchlorates. Fluorine perchlorate [37366-48-6], $FClO_4$, is formed by action of elemental fluorine and 60–70% aqueous perchloric acid solution (68). The compound is normally a gas. It melts at −167.5°C and boils at −15.9°C. It is extremely reactive and explosive in all states.

The perchloryl fluoride [7616-94-6], $FClO_3$, the acyl fluoride of perchloric acid, is a stable compound. Normally a gas having a melting point of −147.7°C and a boiling point of −46.7°C, it can be prepared by electrolysis of a saturated solution of sodium perchlorate in anhydrous hydrofluoric acid. Some of its uses are as an effective fluorinating agent, as an oxidant in rocket fuels, and as a gaseous dielectric for transformers (69).

2.17. Other Transition Element Perchlorates. Both divalent and trivalent manganese perchlorate compounds [13770-16-6; 13498-03-8] are known. Perchlorates of Fe, Co, Ni, Rh, and Pd have been produced as colored crystals (70–72).

The perchlorate ion, $ClO^-{}_4$, is considered to be noncoordinating in the presence of water. When water is rigorously excluded, anhydrous complexes such as $Ni(CH_3CN)_n(ClO_4)_2$, where n is 2, 4, or 6, can be prepared. Perchlorate complexes of Ni, Co, Cu, and Sn have been reported. In each case, however, an organic group such as CH_3CN, CH_3, or pyridyl is involved (73–76).

3. Manufacture

3.1. Perchloric Acid. Several techniques have been employed in the manufacture of perchloric acid, including thermal decomposition of chloric acid (77), anodic oxidation of chloric acid (8), irradiation of chlorine dioxide solutions (78), electrolysis of hydrochloric acid (79), oxidation of hypochlorites by ozone (qv) (80), ion exchange (qv), and electrodialysis of perchlorate salts (81). Perchloric acid is commercially manufactured by reacting saturated solution of sodium perchlorate with hydrochloric acid (9,82). Precipitated sodium chloride is separated from the dilute solution (32% by weight $HClO_4$) by filtration, and the solution is concentrated to 70% by weight via vacuum distillation. Another commercial manufacturing process involves the anodic oxidation of gaseous chlorine dissolved to about 3 g/L in 40% by weight $HClO_4$ at $-5^\circ C$ (83). The electrolysis is carried out in a filter-press-type diaphragm-separated horizontal electrolyzer. Platinum foil titanium anodes and silver cathodes are operated at 2.5–5.0 kA/m^2 (see METAL ANODES). The cell operates at 4.4 V at a current efficiency of 60%. The power required to transfer seven electrons at these conditions is 9600 kWh/t of perchloric acid. The platinum coating dissolves at the anode and redeposits at the cathode at an estimated rate of about 0.025 g/t of 70% perchloric acid. The high purity product manufactured by this process further allows unusual perchlorates to be prepared by direct conversion with perchloric acid.

Highly pure perchloric acid can also be produced by a patented electrochemical process in which 22% by weight hypochlorous acid is oxidized to chloric acid in a membrane-separated electrolyzer, and then additionally oxidized to perchloric acid (8,84). The desired electrochemical oxidation takes place in two stages:

$$2\,H_2O + 4\,HOCl \longrightarrow Cl_2 + 2\,HClO_3 + 6\,e^- + 6\,H^+ \tag{16}$$

$$HClO_3 + H_2O \longrightarrow HClO_4 + 2\,e^- + 2\,H^+ \tag{17}$$

The anode and cathode chambers are separated by a cation-permeable fluoropolymer-based membrane (see MEMBRANE TECHNOLOGY). Platinum-electroplated high surface area electrodes sold under the trade name of TySAR (Olin) (85,86) were used as the anode; the cathode was formed from a two-layer Hastelloy (Cabot Corp.) C-22-mesh structure having a fine outer 60-mesh structure supported on a coarse inner mesh layer welded to a backplate. The cell voltage was 3.3 V at 8 kA/m^2, resulting in a 40% current efficiency. The steady-state perchloric acid concentration was about 21% by weight.

3.2. Perchlorates. Historically, perchlorates have been produced by a three-step process: (*1*) electrochemical production of sodium chlorate; (*2*) electrochemical oxidation of sodium chlorate to sodium perchlorate; and (*3*) metathesis of sodium perchlorate to other metal perchlorates. The advent of commercially produced pure perchloric acid directly from hypochlorous acid means that several metal perchlorates can be prepared by the reaction of perchloric acid and a corresponding metal oxide, hydroxide, or carbonate.

Sodium Perchlorate. The electrochemical oxidation of sodium chlorate is carried out at the anode in an undivided cell according to the following reaction:

$$ClO_3^- + H_2O \longrightarrow ClO_4^- + 2\,H^+ + 2\,e^- \qquad (18)$$

The standard potential for the anodic reaction is 1.19 V, close to that of 1.228 V for water oxidation. In order to minimize the oxygen production from water oxidation, the cell is operated at a high potential that requires either platinum-coated or lead dioxide anodes. Various mechanisms have been proposed for the formation of perchlorates at the anode, including the discharge of chlorate ion to chlorate radical (87–89), the formation of active oxygen and subsequent formation of perchlorate (90), and the mass-transfer-controlled reaction of chlorate with adsorbed oxygen at the anode (91–93). Sodium dichromate is added to the electrolyte in platinum anode cells to inhibit the reduction of perchlorates at the cathode. Sodium fluoride is used in the lead dioxide anode cells to improve current efficiency.

The kinds of cathodes used in industrial electrolyzers are iron, steel, or bronze. The cell tank is always constructed as the cathode and is always negatively charged to prevent cathodic corrosion. In all processes, heat must be removed from the electrolyte either by cooling the internal cell or by circulating through an external heat exchanger. Table 1 gives the operating data for a typical perchlorate cell.

The electrolyte feed to the cells is pretreated to remove impurities, and/or additives are added to the feed to improve cell performance (94). The cell liquor leaving the cell is evaporated, crystallized, and centrifuged to remove solid sodium perchlorate. The clarified cell liquor can undergo reaction in a double metathesis reactor to produce NH_4ClO_4, $KClO_4$, or other desired perchlorates.

A recent patent describes the production of sodium perchlorate by electrolysis of an aqueous solution of sodium chlorate. The solution is subjected to vacuum evaporation. Sodium perchlorate crystals are produced that exhibit good pourability (102). Producers have developed specific cell configurations to optimize electricity consumption, cell capital, and operating costs.

Ammonium Perchlorate. The commercial AP product is manufactured by the double-exchange reaction of sodium perchlorate and ammonium chloride (103,104).

$$NaClO_4 + NH_4Cl \longrightarrow NH_4ClO_4 + NaCl \qquad (19)$$

Ammonia, hydrochloric acid, and sodium perchlorate are mixed and the reaction mixture crystallized in a vacuum-cooled crystallizer. Ammonium perchlorate crystals are centrifuged, reslurried, recentrifuged, and then dried and blended for shipment. Mother liquor is evaporated to precipitate sodium chloride and the depleted mother liquor is recycled to the reactor. The AP product made by this method is 99% pure and meets the specifications for propellant-grade ammonium perchlorate. The impurities are ammonium chloride, sodium perchlorate, ammonium chlorate, and water insolubles.

Extremely high purity ammonium perchlorate can be made by the direct reaction of ammonia and pure perchloric acid solution (8,36):

$$NH_3 + HClO_4 \longrightarrow NH_4ClO_4 \tag{20}$$

The reaction mixture can either be crystallized, centrifuged, and dried, or spray-dried and cyclone-separated to produce a fine crystalline powder having a particle size of 50 μm. Metal analysis of the AP produced by this method is reported to be less than 0.02 μg/g.

4. Shipping and Handling

Perchloric acid and perchlorates are classified as strong oxidizers and emit toxic fumes when decomposed; contact with combustible, flammable, or reducing materials must be avoided. Perchloric acid and perchlorates must be shipped in accordance with the U.S. Department of Transportation hazardous material regulations (105). The maximum shippable quantity, type of packaging, allowable carriers, and other requirements are specified in these regulations. Some perchlorates may not be shipped by a public carrier, passenger-carrying aircraft, or railroad. Handling these compounds requires the procedures and safety precautions specified by the product supplier. Perchlorates contain a self-sustaining source of oxygen, thus fires involving perchlorates must be extinguished with water. A class of more hazardous compounds is formed by mixing inorganic perchlorates with finely divided metals, sulfur, or organic compounds and must be handled with the same precautions as explosives.

5. Economic Aspects

Anhydrous perchloric acid is not sold commercially. Aqueous solutions of perchloric acid are sold at low concentrations for analytical standard applications and at concentrations up to 70%. The price for 70% perchloric acid varies and starts at $2.70/kg, depending on the quantity and level of impurities.

The U.S. production varies, based on the requirements for solid propellants. Environmental effects of the decomposition products, which result from using solid rocket motors based on ammonium perchlorate-containing propellants, are expected to keep increasing public pressure until consumption is reduced and alternatives are developed. NH_4ClO_4-equivalent cell liquor is sold to produce magnesium and lithium perchlorate for use in the production of batteries.

6. Analytical Methods

Thermal decomposition of perchlorate salts to chloride, followed by the gravimetric determination of the resulting chloride, is a standard method of determining quantitatively the concentration of perchlorates. Any chlorates that are present in the original sample also break down to chloride. Thus results are adjusted to eliminate errors introduced by the presence of any chlorides and chlorates in the original sample.

The qualitative determination of water-soluble perchlorates by precipitation using methylene blue yields a violet precipitate (106). Using potassium, rubidium, or cesium salts for precipitation from ethanol–water solutions can serve as a qualitative determination of perchlorates (107). Tetraphenylarsonium chloride (108) has also been used for the precipitation of the perchlorate ion in gravimetric analysis.

Ion-specific electrodes can be used for the quantitative determination of perchlorates in the parts per million (ppm) range (109) (see ELECTROANALYTICAL TECHNIQUES). This method is linear over small ranges of concentration, and is best applied in analyzing solutions where interferences from other ionic species do not occur.

A practical method for low level perchlorate analysis employs ion chromatography. The unsuppressed method using a conductivity detector has a lower detectable limit of about 10 ppm. A suppression technique, which suppresses the conductivity of the electrolyte but not the separated ions, can further improve sensitivity (110,111). Additionally, ion chromatography can be coupled with indirect photometric detection and applied to the analysis of perchlorates (112).

7. Health and Safety Factors

Perchlorates are unstable materials and are an irritant to the body whenever they come in contact with it. Skin contact must be avoided. They are flammable by chemical reaction and are powerful oxidizers. All perchlorates are potentially hazardous when in contact with reducing materials (113).

Perchloric acid is a poison by ingestion and subcutaneous routes. It is a severe irritant to eyes, skin, mucous membranes. Ammonium perchlorate and sodium perchlorate are moderately toxic by ingestion and parenteral routes.

The United States Food and Drug Administration has begun to determine the perchlorate levels in soil, ground water, irrigation water and foods to evaluate any toxic effects. The study is due to be complete in 2005. See Ref. 14 for information.

8. Uses

Perchloric acid is used in analytical chemistry for the determination of trace metal constituents in oxidizable substances as well as in the production of high purity metal perchlorates; it has also been introduced as a stable reaction media in the thermocatalytic production of chlorine dioxide (115). Perchlorates are primarily used in ammonium perchlorate as an oxidizer in the formulations of propellant for solid rocket motors. Perchlorates are used in the production of explosives, pyrotechnics, and in solid, slurried, and gelled blasting formulations. Both magnesium and lithium perchlorates are used in dry batteries. Ammonium perchlorate has been reported as a gas generating component in inflatable restraint systems (116). Other perchlorates have found application in oxygen-generation systems (qv) (117), adhesive bonding of steel plates (118), and the recovery of potassium from brines such as $KClO_4$ (see CHEMICALS FROM BRINE) (119).

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Table 1. **Sodium Perchlorate Cell Operating Information**[a]

current, A	500–5000
current density, kA/m^2	1.5–5.2
cell potential, V	4.8–6.8
anode	PbO_2 graphite, platinum, or Pt on copper
cathode	bronze, stainless steel (316), or iron
anode–cathode spacing, cm	0.2–3
current efficiency, %	90–97[b]; 85[c]
temperature, °C	30–60
pH	6–10
sodium dichromate concentration, g/L	0–5
electrolyte concentration, g/L	
initial	
$NaClO_3$	100–700
$NaClO_4$	0–700
end	
$NaClO_3$	3–100
$NaClO_4$	500–1100
energy consumption, kWh/kg of $NaClO_4$	2.45–3.0
platinum consumption, g/t of $NaClO_4$	2–7
operation mode	batch or continuous

[a] Refs. (92–101).

[b] Pt anodes.

[c] PbO_2 anodes.