PERCHLORIC ACID AND PERCHLORATES

by

ALFRED A. SCHILT
Department of Chemistry
Northern Illinois University
DeKalb, Illinois 60115

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G. FREDERICK SMITH

An inspiring mentor, zealous researcher, delightful raconteur.
and faithful friend.

ABOUT THE AUTHOR

Alfred A. Schilt is Professor of Chemistry at Northern Illinois University where he has taught and conducted research in analytical chemistry since 1962. He completed both his undergraduate studies and a masters degree at the University of Colorado before joining the Eastman Kodak Company as an analytical chemist in 1951. Two years later he resumed graduate studies at the University of Illinois where, under the enthusiastic direction of Professor G. Frederick Smith, he developed strong abiding interests in perchloric acid and perchlorate chemistry, spectrophotometric reagents for trace metal determinations, and applications of coordination chemistry in chemical analysis. After receiving his doctorate in 1956 he taught at the University of Michigan until 1962 when he joined the faculty at Northern Illinois University. In addition to numerous research articles, he is the author of "Analytical Applications of 1,10-Phenanthroline and Related Compounds" published by Pergamon Press in 1969 and co-author of "The Copper Reagents: Cuproine, Neocuproine, Bathocuproine" published by The G. Frederick Smith Chemical Company in 1972.

PREFACE

This monograph is intended to serve as a ready, single source of useful information on the chemistry and applications of perchloric acid and perchlorate compounds. It should also prove helpful to those who would contribute further to the knowledge and utilization of these versatile and intriguing compounds. To this end a thorough search has been made of the literature up to and including publications in 1977. Most, if not all, of the pertinent references are cited. This approach, coupled with a desire for conciseness, has precluded an in-depth treatment of many of the topics. Many papers related to the study of the compounds for use in explosives and propellant mixtures have been omitted. Also omitted for the most part are references to research articles that employed or dealt only marginally with perchloric acid or its salts.

Over the more than 160 years since its inception an aura of fear highlighted by general ignorance or lack of reliable information has surrounded perchloric acid chemistry. Thanks to the pioneering efforts and energies of scientists such as G. Frederick Smith, H. H. Willard, and their many devoted students, perchloric acid and its compounds are now widely and effectively employed. Fear and ignorance have given way to respect and understanding, with due regard for appropriate safety measures. It is sincerely hoped that this monograph will help disseminate the knowledge and safeguards to enable others to put perchloric acid and its derivatives safely and effectively to work in solving their particular problems.

ALFRED A. SCHILT

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CHAPTER I

INTRODUCTION

Historical Highlights

The first preparation of a perchlorate compound was described by Count Friederich von Stadion in a paper entitled "Von den Verbindungen des Chlorine mit dem Sauerstoff", published in 1816.[1] He obtained a new salt, which he called "oxygenated potassium chlorate", as a water-insoluble residue from a mixture of potassium chlorate and concentrated sulfuric acid which had been allowed to stand for 24 hours with frequent agitation. In the same paper he also described obtaining "oxygenated chloric acid" by distilling a mixture of the new salt with its own weight of sulfuric acid (diluted with one-third its weight of water) to 140°, collecting the white vapors that condense in the receiver as a liquid acid. His "liquid acid" was undoubtedly an aqueous solution containing approximately 70% by weight perchloric acid. In a subsequent 1818 paper,[2] Stadion described electrolytic methods for preparation of "oxygenated chloric acid" and "oxygenated potassium chlorate".

Important contributions were made in the early 1830's by G. S. Serullas who prepared ammonium perchlorate, a number of metal perchlorates, and a solid form of perchloric acid (mistaken for the anhydrous acid but later identified as the monohydrate).[3-5] Serullas also introduced the term "perchlorate", using it interchangeably with Stadion's term "oxychlorate".

In the thirty-year period following the work reported by Serullas, a number of significant papers appeared describing new preparations of perchlorates and perchloric acid. These included contributions by Berzelius in 1835,[6] by Penny in 1840,[7] and by Kolbe in 1862.[8] The preparation of ethyl perchlorate, an extremely hazardous explosive, was reported in 1841 by Hare and Boye.[9] Anhydrous perchloric acid, another very explosive substance, was prepared in 1862 by Roscoe,[10] who also correctly identified the solid acid obtained by Serullas as the monohydrate.[11]

The explosive nature of certain perchlorates undoubtedly discouraged many from undertaking further studies. Still others were attracted by the possible commercialization of perchlorates for use in pyrotechnics and explosives. For example, Swedish patents were issued to O. F. Carlson in 1892[12] and 1897[13] relating to the manufacture of explosives containing perchlorates. The first commercial perchlorate plant was constructed in 1893 at Mansbo, Sweden. Production problems were numerous and slow to be resolved, but by 1904 the plant was producing ammonium perchlorate on an efficient, regular basis.[14] Not long afterwards manufacture of sodium, potassium, and ammonium perchlorates began in other countries, notably France, Switzerland, Germany and the United States. Production was pushed to maximum levels during World Wars I and II. Instead of falling as it did after World War I, production of ammonium perchlorate continued to grow after 1945, increasing phenomenally in the 1950's because of its usefulness in solid rocket propellants.[14] The remarkable commercial growth for perchlorates from 1910 to the present was accompanied or preceded quite naturally by comparable growth in research. Numerous patents were granted, and countless research publications appeared. Research activity, as evidenced by rate of publication, continues strong to this day.

In reviewing the history of any endeavor the contributions of certain individuals can be seen clearly in retrospect to have influenced significantly further progress and work by others. In addition to recognizing the pioneering efforts of Stadion, Serullas and Roscoe, any historical account of perchloric acid and perchlorates should include at least mention of the persons and contributions cited in the following sentences. Isolation of the anhydride of perchloric acid, Cl_2O_7, was achieved by A. Michael and W. T. Conn in 1900.[15] Extensive measurements of physical properties of perchloric acid-water mixtures were reported in 1902 by H. J. van Wyk leading to the identification of five separate hydrates.[16] In 1912, H. H. Willard of the University of Michigan described a convenient and practical method for the preparation of perchloric acid from ammonium perchlorate.[17] Assisted by various graduate students, Professor Willard made a number of significant contributions to perchlorate chemistry in the course of his long and remarkably productive career.[18] Possibly the most significant influence that Willard exerted on the advancement of perchlorate chemistry was to interest G. Frederick Smith, one of his first graduate students, to undertake his doctoral research on the subject. From his earliest publication with Willard in 1922 to his last professional publications in 1966, and even up to his death in 1976, Smith never lost his curiosity and enthusiasm for perchlorate chemistry research. With over 60 research papers and publications devoted to the subject, he had truly a lifelong love affair with perchlorate chemistry. In addition to advancing the use of perchloric acid and perchlorates in chemical analysis, Professor Smith carried out fundamental studies, devised new preparation procedures, and founded the chemical company that bears his name and has provided perchloric acid and perchlorates to the scientific community since 1928.[19]

In the early 1930's Ernest Kahane of Paris, France published a number of important papers describing the use of perchloric acid for the total destruction of organic and biological matter prior to determination of mineral constituents. Many investigations and applications followed after Kahane's original publication.[20] More recent contributions to perchlorate chemistry include the preparation of perchloryl fluoride by Bode and Klesper[21] and the preparation of chlorine and bromine perchlorates by Schack, Pilpovich, and Wilson.[22] These perchloric acid derivatives have proven useful in organic synthesis.

Question of Natural Occurence

The discovery of small amounts of perchlorates in natural deposits of nitrates in Chile was reported by Beckurts in 1886.[23] This was confirmed a number of years later by various groups of investigators concerned with the possible harmful effects of perchlorate in Chilean nitrate used as plant food.[24-27] In 1896 Sjollema reported finding potassium perchlorate as a contaminate of Chile saltpeter in amounts ranging from 0 to 6.79%, varying even within the same lot.[25] Maschhaupt found a maximum perchlorate content of 1.5% in crude and about 1% in refined saltpeter.[27] Questions as to how the perchlorate was produced by natural means and why perchlorate has been found naturally only in Chilean saltpeter remain disturbingly unanswered. It is possible that the answers could provide new insights into geological and biological processes and even lead to a new method of preparation of perchlorates.

Discovery of perchlorate in sea water was reported in 1958 by Baas-Becking, Haldane, and Izard,[28] who found levels of 10 to 1000 ppm ClO_4 in samples collected at various localities. Their findings have not been substantiated but instead rather strongly refuted by others. An extensive study by Greenhalgh and Riley[29] indicated no detectable concentration of perchlorate in any of over 30 surface and deep-water samples collected from both northern and southern hemispheres[30] *They attributed the earlier findings of Baas-Becking and co*workers to chloride interference. Johannesson[31] found no evidence of naturally occuring perchlorates in samples of fresh-seawater taken 50 miles apart off the coast of Wellington, New Zealand in 1960. At least two other groups have reported the absence of detectable levels of perchlorate in sea water samples, based upon highly sensitive analytical procedures.[32,33] Thus it appears that perchlorate is not an important natural constituent of sea water.

Structure and Properties of Perchlorate Ion

X-ray diffraction measurements on crystalline hydronium perchlorate by Lee and Carpenter[34] indicate that the perchlorate ion has nearly perfect tetrahedral geometry and an average Cl-O bond distance of 1.42 Å. In water its limiting conductance is 67.32 ± 0.06.[35] A difference in molar refractive power between perchlorate ion and chloride ion of 6.66 ± 0.06 has been deducted from refractive index measurements of their aqueous solutions.[36] The standard enthalpy of formation of the perchlorate ion in infinitely dilute aqueous solution at 25° has been determined by two *different groups of investigators; their results —30.53 ± 0.20*[37] and —30.87 ± 0.07 kcal/mole[38] are in close agreement.

X-ray photoelectron spectra[39] and fluorescence spectra[40] have been investigated to study the bonding and electronic structure of the perchloric anion. The results indicate that the

3d-orbitals of chlorine participate in the $3d_\pi(Cl)$-$2p_\pi(0)$ and $3d_\sigma(Cl)$-$2s(0)$ bonds. The relative contributions of the chlorine 3d-orbitals to the 6- and II- bond levels were evaluated by comparing relative intensities in the L-spectrum of chlorine.[40]

The hydration number of the perchlorate ion has an average value of 4, according to Symons and Waddington[41] who based their determination upon Raman and infrared spectra of aqueous solutions. They found a similar value for the fluoroborate anion. It appears that each oxygen atom, or fluoride atom in the case of fluoroborate, may be hydrogen bonded by a separate water molecule. Hydration of perchlorate ions in nitrobenzene has been studied using cryoscopic measurements to estimate the value of the first hydration constant.[42] Solvation in methanolic solutions has also been studied by low temperature infrared spectroscopy.[43] Raman spectra of various aqueous perchlorate solutions have been interpreted and evaluated as a function of concentration to study the state of perchloric ions and their interactions with metal ions.[44]

The effect of perchlorate ions on the hydrogen bonded structure of water has been examined by infrared spectrometry.[45,46] *Strong evidence of the breaking of water structure by perchlorate ions was found with the observation that the optical density of the 2100 cm*$^{-1}$ *band (combination band of* H_20*) decreases with increasing perchlorate ion concentration, while that of the 3590 cm*$^{-1}$ *band (fundamental band of* H_20*) increases. No detectable absorption was observed in the 4000-600 cm*$^{-1}$ *region indicative of hydrogen bonding between water and perchlorate ion, and the fundamental band due to perchlorate ion was unaltered. This suggests that the interaction which causes the water structure to be altered is purely ionic.*[45]

Nuclear magnetic resonance studies of perchlorate solutions have provided some insights concerning the interactions of perchlorate ions with solvent and with metal cations. Berman and Stengle[47] found that free perchlorate ions in solution have a longer relaxation time than in a contact ion-pair with cations, as indicated by NMR line widths for chlorine-35. They report that the tendency for perchlorate ions to form contact ion-pairs is favored by high charge to radius ratio of cation, low dielectric constant of solvent, and low basic strength of solvent. Craighead and Bryant[48] found evidence of weak complexation between manganous and perchlorate ions. Based upon chlorine-35 NMR relation time measurements they estimated an exchange rate of 3×10^4 to 3.6×10^7 sec^{-1} for the perchlorate-manganous ion exchange process. Quadrapole relaxation studies of perchlorate and other tetrahedral ions in aqueous solution have been reported also by Reimarsson and coworkers.[49] A proton magnetic resonance study of the interaction of perchlorates with anhydrous perchloric acid has provided evidence of hydrogen bonded $H(ClO_4)_2^-$ anion formation.[50]

Although the basicity of the perchlorate ion is exceedingly weak, it is capable of metal ion complexation in the absence of excessive competition by solvent or other ligands. Considerable evidence now supports this once widely doubted fact.[51,52] Further details are provided in Chapter III.

Oxidation-reduction and other chemical properties of the perchlorate ion are described together with those of the acid and other perchlorate compounds in the chapters that follow.

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CHAPTER II

PREPARATION AND PROPERTIES OF PERCHLORIC ACID

AQUEOUS PERCHLORIC ACID

Preparation

Perchloric acid was first synthesized by von Stadion[1,2] in 1816 by vacuum distillation of a mixture of sulfuric acid and potassium chlorate, and by electrolysis of a saturated aqueous solution of chlorine dioxide. Numerous other methods have been devised since, however the most important commercial ones are based upon either the Kreider-Mathers[3] or the Willard[4] method. These and other methods, classified as to type, are described below.

Electrosynthesis. Electrolytic oxidation of hydrochloric acid to perchloric acid, as described by Walker[5] in 1918 and in greater detail by Goodwin and Walker[6] in 1921, proved relatively inefficient for commercial purposes. Production of chlorine rather than perchloric acid is favored at higher concentrations of hydrochloric acid, so it is necessary to employ very dilute (0.1-0.5 N) solutions and thus extensive evaporation to concentrate the product. Some improvements were forthcoming. Rakov and coworkers[7] found that (1) perchloric acid formation begins at 2.4 V and reaches a maximum value at 2.8-2.9 V, (2) lowering the temperature to —20° significantly accelerates the process, and (3) concentration changes of chloride ion from 0.5 to 1.8 N and of perchlorate ion from 3 to 8 *N* are without effect except for decreased current efficiency at the highest concentration of hydrochloric and perchloric acid. In another study, Rakov *et al.*[8] found that platinum anodes afford higher yields of perchloric acid than did Pt-Ti or Pt-Ta bianodes. Rakov and Shimonis,[9] in a patent granted in 1976, claim increased current efficiency is attained in the electrosynthesis of perchloric acid from 1 to 4 N hydrochloric acid by using an iridium anode at a potential of 2.9-3.3 V and a temperature at —5 to —30°.

Preparation by anodic oxidation of chlorine has been investigated.[10] At platium electrodes a reaction apparently occurs between adsorbed chlorine and active oxygen which leads to formation of perchloric acid through an adsorbed intermediate product.[11] Lead dioxide anodes are especially effective, particularly if sodium flouride is added to the electrolyte.[12]

Electrolytic oxidation of chlorates was investigated by Newman and Mathers.[13] Using a two-diaphragm, three-compartment cell with a platinum anode and iron cathode they were able to obtain an aqueous solution of about 2 N perchloric acid prior to concentrating by evaporation.

Double-decomposition. A solution of perchloric acid can be made by warming an aqueous solution of potassium perchlorate with a small excess of hydrofluosilicic acid, H_2SiF_6, for an hour, and filtering the cooled liquid.[14,15] The slight excess of H_2SiF_6 can be removed by adding a little barium perchlorate or chloride. Another preparation involves decomposition of barium perchlorate with sulfuric acid to yield insoluble barium sulfate and perchloric acid.[16] Kreider[17] prepared an aqueous solution of perchloric acid by treating sodium perchlorate with an excess of concentrated hydrochloric acid, filtering off the sparingly soluble sodium chloride, and heating to 135° to drive off the excess hydrochloric acid. Mathers[18] investigated the Kreider procedure and provided additional procedural details. The Kreider-Mathers method of preparation proved suitable for commercial use and led to the Pernet process,[19] patented in 1946, which provides for continuous operation and nearly automatic control.

A mixture of potassium perchlorate and sulfuric acid when distilled in a current of steam yields an aqueous solution of perchloric acid, contaminated by sulfuric acid, which must be redistilled or treated with barium carbonate to remove sulfate.[20] A much superior method, devised by Willard,[4] involves treatment of ammonium perchlorate with an excess of a mixture of nitric and hydrochloric acid, giving rise to the approximate over-all reaction as follows:

$34\ NH_4ClO_4 + 36\ HNO_3 + 8\ HCl \rightarrow 36\ HClO_4 + 4\ Cl_2 + 35\ N_2O + 73\ H_2O$. Gaseous products and any excess acid reactants are eliminated on heating to concentrate the perchloric acid to its constant boiling composition. Yields in excess of 99%, approaching theoretical, were obtained by Willard.

Chemical Oxidation. Ozone can be used to oxidize hypochlorous[21] and chloric acid[22] to perchloric acid. Patents have been issued for the production of perchlorates and perchloric acid by ozone treatment of chlorates in $HClO_4$[23]and of gaseous mixtures of water and chlorine or hydrogen chloride irradiated with 2537 Å.[24]

Chloric acid undergoes self-oxidation, especially if concentrated, decomposing into perchloric and chlorous acids.[25] Serullas obtained perchloric acid in low yield from thermal decomposition of chloric acid.[26]

Preparation procedures for perchloric acid and perchlorates by oxidation of chloric acid or chlorates on heating with silver oxide[27] or by oxidation with lead dioxide in 55-70% H_2SO_4[28] have been reported but appear to afford little advantage.

Purification

Aqueous solutions of perchloric acid can be concentrated by boiling at atmospheric pressure to 203°, at which point an azeotropic solution is attained containing 72.4% $HClO_4$. For purification by distillation it is necessary to employ reduced pressures (below 200 mm) to avoid partial decomposition to chlorine, chlorine oxides and oxygen. Distillation procedures are described in papers by Mathers,[3] Willard,[4] and others.[29-31]

High-purity perchloric acid (70% by weight), greatly diminished in trace metal content, can be conveniently prepared by a sub-boiling distillation method developed at the National Bureau of Standards.[32] A production rate of about 600 ml of perchloric acid per day was achieved using a pure quartz sub-boiling still. Analysis revealed the presence of 16 ppb total impurity elements as opposed to 3400 ppb for the ACS grade starting acid and 100 ppb for a commercial high-purity acid. Using a similar appartus, but with a constant-level feed-control device, other workers[33] decreased lead impurities in 70% perchloric acid to levels of 0.2-0.4 ppb in a single pass.

An interesting method for removal of impurities from 1 M perchloric acid for use as a supporting electrolyte has been described,[34] based upon adsorptive and electroctive properties of a column of platinum sponge held at a fixed potential.

Physical Properties

Extensive measurements have been made of the physical properties of aqueous solutions of perchloric acid, particularly by H. J. Van Wyk and by L. H. Brickwedde. These are summarized briefly with literature references in the following paragraphs, and many of the results are compiled in Tables 1 through 8.

Densities of aqueous solutions at various temperatures have been reported by Van Wyk,[35] Brickwedde,[36] Clark,[37] van Emster,[38] Markham,[39] and Smith.[40] Tables 1 and 2 include most of the results.

Freezing point data were determined and plotted versus composition by Van Wyk[35,41] and by Brickwedde[36] to identify hydrates.

Vapor pressures and activity coefficients were measured by Pearce and Nelson,[42] Robinson and Baker,[43] and Robinson and Stockes.[44] Results are compiled in Tables 3 and 4. Boiling points of various aqueous compositions are listed in Table 5.

Viscosities are reported by Brickwedde,[36] Van Wyk,[35] Clark,[37] and Simon.[45] Table 6 includes the data.

Surface tension data of Neros and Eversole,[46] given in Table 7, indicate that a maximum occurs at a composition corresponding to $HClO_4 \cdot 3H_2O$.

Refractive index measurements are reported by McLean and Pearson[47] for perchloric acid solutions of 0 to 72 per cent concentration at 20° and 30°. Their data are compiled in Table 8 and provide a convenient means of determining concentration of aqueous perchloric acid solutions. A plot of molar refraction against acid concentration yields a smooth curve with a minimum at 18% $HClO_4$.[48-49] From density and refractive index data, a radius for the perchlorate ion of 1.82 Å[51] and apparent molal volumes[48-50] were calculated.

Electrical resistivity and conductance measurements have been reported by Brickwedde[36] of solutions 10 to 70 weight per cent perchloric acid from —60 to +50° C, by Usanovich and Sumarokova[52] for 0 to 100% $HClO_4$ at 50°, and by Klochko and Kurbanov.[53] Discontinuities in the specific conductance curves corresponding to tri- and tetrahydrates and a maximum at 37 weight per cent $HClO_4$ were found[52,53]. Viscosity and electrical conductance of perchloric acid solutions from —50 to +90°C were reported recently by Maksimova *et al.*[54] Conductance, transport numbers, diffusion coeffients, and related quantities have been reported for aqueous perchloric acid at 25° C by Haase.[55]

TABLE 1. DENSITIES OF AQUEOUS PERCHLORIC ACID SOLUTIONS[36]

$HClO_4$	Density (g/ml) at Various Temperatures (°C)							
Wt. %	40°	30°	25°	20°	10°	0°	—10°	—20°
0	0.992	0.996	0.997	0.998	1.000	1.000	....	....
5	1.020	1.024	1.026	1.027	1.029	1.031	....	....
10	1.050	1.054	1.056	1.058	1.061	1.064	....	....
15	1.081	1.086	1.088	1.091	1.095	1.099	1.102	....
20	1.114	1.120	1.123	1.125	1.131	1.136	1.140	....
25	1.150	1.157	1.160	1.163	1.169	1.175	1.180	....
30	1.189	1.196	1.200	1.204	1.210	1.217	1.223	1.228
35	1.232	1.239	1.244	1.247	1.255	1.262	1.266	1.275
40	1.278	1.286	1.291	1.294	1.303	1.311	1.318	1.326
45	1.329	1.338	1.343	1.347	1.356	1.366	1.375	1.384
50	1.385	1.395	1.400	1.405	1.415	1.425	1.436	1.447
55	1.445	1.456	1.462	1.467	1.478	1.490	1.502	1.514
60	1.510	1.521	1.527	1.533	1.545	1.558	1.571	1.584
65	1.578	1.590	1.596	1.603	1.616	1.629	1.643	1.656
70	1.645	1.658	1.664	1.672	1.685	1.699	1.712	1.725

TABLE 2. SPECIFIC GRAVITY OF PERCHLORIC ACID SOLUTIONS[35]

$HClO_4$		Specific Gravity	
Mole %	Weight %	20°C	50°C
100	100	1.7676	1.7098
92.75	98.62	1.7817	1.7259
76.15	94.69	1.8059	1.7531
63.85	90.78	.....	1.7690
50.00	84.80	.....	1.7756
43.4	81.06	.....	1.7619
35.67	75.57	1.7386	1.7023
27.96	68.41	1.6471	1.6110
21.44	60.37	1.5353	1.5007
15.46	50.50	1.4078	1.3779
10.56	39.72	1.2901	1.2649
6.23	27.05	1.1778	1.1574

TABLE 3. VAPOR PRESSURE OF PERCHLORIC ACID AQUEOUS SOLUTIONS AT 25°C[42]

Molality $HClO_4$	Vapor Pressure, mm
0.0	23.752
0.20064	23.593
0.60655	23.254
1.01589	22.870
3.1512	20.192
5.4347	16.308
7.8719	11.490
10.5139	6.838

TABLE 4. MEAN ACTIVITY COEFFICIENTS AND OSMOTIC COEFFICIENTS OF AQUEOUS PERCHLORIC ACID SOLUTIONS AT 25 °C[43]

$HClO_4$ Molarity	Activity Coefficient $f_\pm$	Osmotic Coefficient f_0
0.2	0.766	0.951
0.4	0.754	0.966
0.6	0.763	0.988
0.8	0.784	1.013
1.0	0.810	1.041
2.0	1.039	1.210
3.0	1.420	1.406
4.0	2.018	1.622
5.0	2.94	1.860
6.0	4.41	2.106
7.0	6.90	. .
8.0	11.32	. .
9.0	18.0	. .
10.0	29.0	. .
11.0	47.3	. .
12.0	77.7	. .

TABLE 5. COMPOSITION OF LIQUID AND VAPOR PHASES OF AQUEOUS PERCHLORIC ACID AT DIFFERENT BOILING POINTS

Boiling point °C	Pressure mm	Weight per Cent $HClO_4$	
		Liquid	Vapor
203	760	72.40	72.40
198.7	760	70.06	40.11
181.2	760	65.20	6.06
162.3	760	61.2	0.90
148.0	760	56.65	..
114.8	760	38.90	..
107	18	70.5	..
92	18	79.8	..
70	18	84.8	..
35	18	92.0	..
24.8	18	94.8	..
16.0	18	100	..
39	56	100	..

TABLE 6. ABSOLUTE VISCOSITY OF AQUEOUS PERCHLORIC ACID SOLUTIONS[36]

$HClO_4$	Absolute Viscosity (centipoises)* at Various Temperatures (°C)							
Wt. %	40°	30°	25°	20°	10°	0°	—10°	—20°
0	0.653	0.798	0.890	1.002	1.306	1.786	2.59	....
5	0.662	0.803	0.894	1.004	1.287	1.743	2.47	....
10	0.675	0.813	0.901	1.010	1.280	1.714	2.40	....
15	0.692	0.829	0.913	1.022	1.286	1.701	2.347	....
20	0.715	0.853	0.937	1.043	1.307	1.707	2.329	....
25	0.750	0.890	0.974	1.080	1.347	1.745	2.353	....
30	0.794	0.940	1.031	1.139	1.413	1.815	2.434	3.415
35	0.859	1.013	1.108	1.223	1.514	1.925	2.572	3.581
40	0.950	1.118	1.224	1.345	1.670	2.113	2.814	3.928
45	1.080	1.274	1.395	1.534	1.900	2.426	3.244	4.582
50	1.271	1.507	1.650	1.821	2.268	2.914	3.962	....
55	1.548	1.837	2.022	2.237	2.819	3.677	5.104	7.570
60	1.928	2.296	2.532	2.813	3.560	4.713	6.700	9.962
65	2.440	2.913	3.211	3.560	4.523	5.969	8.40	12.37
70	3.094	3.692	4.060	4.504	5.675	7.333	9.92	14.19

*Based upon absolute viscosity of water at 20°C=1.002 centipoises.

TABLE 7. SURFACE TENSION OF PERCHLORIC ACID SOLUTIONS[46]

$HClO_4$ Weight %	Surface Tension at Various Temperatures (°C) 15°	25°	50°
0.00	73.51	71.97	68.16
4.86	72.52	71.18	67.60
10.01	71.66	70.34	66.97
20.38	70.46	69.21	66.12
30.36	69.82	68.57	65.66
40.37	69.72	68.49	65.74
53.74	70.33	69.02	66.60
60.70	70.88	69.69	67.40
63.47	70.77	69.73	67.44
67.59	70.67	69.71	67.41
70.43	70.07	69.54	67.26
72.25	69.96	69.01	66.85

TABLE 8. REFRACTIVE INDEX OF AQUEOUS PERCHLORIC ACID[47]

$HClO_4$ Weight %	Refractive Index 20°C	Refractive Index 30°C
0.00	1.3330	1.3320
9.73	1.3395	1.3381
20.05	1.3470	1.3452
30.75	1.3580	1.3559
40.31	1.3680	1.3665
50.28	1.3813	1.3800
60.08	1.3983	1.3960
62.81	1.4034	1.4010
64.00	1.4054	1.4028
68.52	1.4129	1.4103
70.06	1.4151	1.4130
72.62	1.4190	1.4159

Raman spectra[56,57] and proton magnetic resonance spectra[58] *have been recorded to study the degree of dissociation of* perchloric acid in aqueous solutions.

Apparent molal expansibility, volume, and compressibility of aqueous solutions of perchloric acid at 25° were determined recently[59] to study their dependence on composition *and the nature of anion interactions with water.*

Chemical Properties

The chemistry of perchloric acid in aqueous solutions can be characterized briefly as that of an exceptionally strong acid with essentially no oxidizing strength except towards active metals that normally displace hydrogen from acids. However, if the perchloric acid be both hot and concentrated *its oxidizing properties are considerable, and in certain cases* dangerously vigorous. It is also a strong dehydrating agent when hot and concentrated. Under such conditions it serves as an highly efficient oxidant for destruction of organic matter. When dilute or cold, however, its oxidizing strength is so greatly diminished that it is suitable for use without interference in the study of many redox reactions. Likewise, the *very weak tendency for perchlorate ions to coordinate to* metal ions favors the use of perchloric acid as a non-interfering acid in complexation studies.

Perchloric acid is one of the strongest acids known. Its effective strength depends, like any other acid, on the basicity *of the solvent in which it is dissolved. In water it is* completely ionized in the most concentrated solutions and completely dissociated up to a concentration of about 4 M, where the first appearance of undissociated $HClO_4$ has been detected.[60] In concentrated sulfuric acid it is strongly dissociated but weaker than disulfuric acid ($H_2S_2O_7$).[61] In organic solvents it behaves as a strong acid, highly ionized but not necessarily highly dissociated, depending on dielectric and solvation strengths of the solvent. As a strong acid it is especially useful in measuring pK values and relative strengths of very weak bases. Hammett acidity functions for this purpose have been measured by various workers, including Gillespie,[62] Yates *et al.*,[63,64] *and Attiga and Rochester.*[65] Values of the acidity function, H_0, for perchloric acid in acetic acid-water mixtures have been determined by Wiberg and Evans.[66]

Certain strong reductants are oxidized by perchloric acid at room temperature. Increasing the concentration of perchloric acid favors its reaction rate as an oxidant, suggesting that the protonated form rather than the perchlorate ion is the active species.[67] Some of the reductants investigated in reaction rate studies include ruthenium(II),[68] titanium(III),[69] molybdenum(III),[70] chromium(II),[70] titanous chloride or sulfate,[17] platinum cathode,[72] hydrogen and simple organic fuels,[73] and various metals.[74] Reductants for perchlorates are further discussed in Chapter VII.

Perchloric acid solutions are decomposable thermally or by exposure to ionizing radiation. Studies of its thermal decomposition indicate an activation energy for decomposition of 22.56 kcal/mol[75], an autocatalytic effect for 65-100 wt % $HClO_4$,[76] and heterogeneous catalysis by oxides of iron, copper or chromium.[77] Radiolysis studies reveal that perchloric acid decomposes only as a result of direct action of the radiation, yielding chlorate ions as major product, and that it does not react with products from the radiolysis of water.[78-80]

HYDRATES OF PERCHLORIC ACID

A total of five different hydrate compositions have been identified from studies of liquid-solid equilibriums in the binary system perchloric acid-water. Several different investigators confirm these findings. Van Wyk,[35,41] the first to investigate the system, found the following hydrates: $HClO_4 \cdot H_2O$, $HClO_4 \cdot 2H_2O$,, $HClO_4 \cdot 2.5H_2O$, α- and β-forms of $HClO_4 \cdot 3H_2O$, and $HClO_4 \cdot 3.5H_2O$. Brickwedde[36] obtained a freezing point-composition plot very similar to that of Van Wyk's but with different, presumably more accurate, temperatures. Zinov'ev and Babaeva[81] confirmed the existence of all five hydrates, noting also that the mono- and dihydrate exist in aqueous solution up to a temperature of 75° and that the other three hydrates are much more highly dissociated. Mascherpa and coworkers,[82] on repeating the study of Van Wyk over the concentration range of 58-74 wt. per cent $HClO_4$, found hydrates of 1 molecule of $HClO_4$ with 2, 2.5, 3, and 3.5 molecules of H_2O, exhibiting melting points respectively of —20.65°, —32.1°, —40.2°, and —45.6° (all ± 0.1°). A sixth hydrate composition, corresponding to $H_2O \cdot 4HC1O_4$, has been reported by Mascherpa,[84] based upon a thermal analysis study.

Perchloric acid hydrates involve considerable hydrogen bonding. A bond-valence analysis of five of the hydrates by Brown[84] shows that normal H-bonds account for only about *one-half of the bonding of the perchlorate ion. Each H-atom* also forms an average of four additional weak interactions. The infrared spectrum of crystalline perchloric acid trihydrate is consistent with H_30^+ central pattern complexed by two water molecules through short asymmetric hydrogen bonds.[85] Perchlorate ions participate to some extent in hydrogen bonding in the hydrate $HClO_4 \cdot 3.5\ H_2O$ according to Almlof.[86] For this hydrate, X-ray diffraction data[86] at —188° indicates two independent $H_9O_4{}^+$ complexes having one water *molecule in common. The two perchlorate ions show only* minor deviations from tetrahedral symmetry, with mean Cl-O distances of 1.437 and 1.443 Å.

The most extensively studied hydrate is the monohydrate. It exists entirely as the oxonium salt $H_3O^+ClO_4$ and thus can be correctly referred to as oxonium perchlorate. It contains 84.78 per cent $HClO_4$ by weight, forms long needle-like crystals, melts at 49.905° with considerable expansion, and exhibits a heat of fusion of 2.46 ± 0.08 kcal/mole. Methods for its preparation, described by Roscoe[87] and by Klages,[88] involve preparation of the anhydrous acid and treatment with an appropriate amount of either water or perchloric acid dihydrate. Oxonium perchlorate dihydrate can be safely stored at room temperature indefinitely without decomposition if protected from reactive substances.

The crystal structure of oxonium perchlorate has been determined by X-ray diffraction.[89] A reversible phase change occurs —23.4° accompanied by an increase in density.[90] Below this temperature, at —80° Nordman[91] reports that the crystal structure belongs to the monoclinic space group and consists of H-bonded layers of perchlorate and hydronium ions. Above the transition point the structure is orthorhombic and more disordered. The perchlorate ions are nearly perfect tetrahedra with an average Cl-O distance of 1.42 Å. Proton magnetic resonace spectra[92] indicate that the oxonium ion has a pyramidal structure. The Raman spectrum[93] is consistent with the X-ray and NMR findings, and valence force constants have been calculated.

Dioxonium perchlorate (perchloric acid dihydrate, 73.60 wt. % $HClO_4$) boils at 203° at atmospheric pressure, is hygroscopic, fumes in moist air, and freezes at —17.8°. Recommended as a primary standard for acidimetry,[40] it can be prepared by distilling 70-72% $HClO_4$ at 2-7 mm and discarding the first-half or more of the distillate before collecting the dioxonium perchlorate.

ANHYDROUS PERCHLORIC ACID

Preparation and Properties

The preparation of anhydrous perchloric acid can be readily achieved by fractional distillation of a mixture of concentrated sulfuric acid and 65-70% perchloric acid.[94,95] Magnesium perchlorate,[96] phosphorous pentoxide,[97] and sulfur trioxide[97] have also been described as dehydration agents in place of sulfuric acid. Anhydrous perchloric acid can also be obtained by extration into methylene chloride from a mixture of one part by volume of 70% perchloric acid and four parts 25% fuming sulfuric acid.[88] It has been recommended that only small amounts of reagents be used in this procedure and that the extraction flask be kept cold because of the risk of an explosion.[98] Procedures for the preparation of anydrous deuterium perchlorate and D_3OClO_4 have been described by Smith and Diehl.[99]

The anhydrous acid is colorless, hygroscopic, volatile, extremely reactive, and explosively unstable. In contact with skin it produces serious and painful wounds. On addition to water it generates considerable heat and a hissing noise. It freezes at —112° and boils at 18 mm at 16° without decomposition. It can not be distilled at ordinary pressures without decomposition and explodes at about 90°. On standing at ordinary temperatures the pure acid gradually yellows and eventually (within 10 to 30 days) explodes spontaneously. Storage time can be extended up to 60 days by use of liquid-air temperatures without formation of colored decomposition products. Extreme caution is necessary to avoid contacting the anhydrous acid with wood, paper, or other combustible matter because explosions invariably result, even at ordinary temperatures. Except for special use or need anhydrous perchloric acid should not be made or stored.

*Anhydrous perchloric acid undergoes partial autodis*sociation to chlorine heptoxide and oxonium perchlorate above its melting point, and the rate of attainment of equilibrium increases rapidly above —30°.[100] The existence of the equilibrium 3 $HClO_4 \rightleftarrows Cl_2O_7 + HClO_4 \cdot H_2O$ has been demonstrated from viscosity,[101] kinetics of decomposition and vapor pressure,[102] and electrical measurements.[103] Rosolovskii[102] reports values for the equilibrium constant (as written above) *of* 0.80×10^{-4} *at* —10°, 1.30×10^{-4} *at* 20°, *and* 1.94×10^{-4} *at* 70°. Bout and Potier[103] report a value of 0.60×10^{-6} for the self-dissociation equilibrium constant of the following reaction:

$$3\ HClO_4 \rightleftarrows ClO_2O_7 + H_3O^+ + ClO_4^-$$

This value differs from Rosolovskii's because of the difference in formulating the oxonium perchlorate product. The *extent of self-dissociation is thus indicated in either formula*tion at approximately 1 per cent.

Heat capacities and thermodynamic functions for anhydrous perchloric acid from 5 to 55°K indicate that $HClO_4$ exists as an independent species in the crystalline state.[104] At 298.15 °K its heat capacity, C_P, is 28.80 cal/mol degree. A triple point occurs at 172.0 °K.

Raman and infrared spectra of anhydrous $HClO_4$ and $DClO_4$ *have been extensively studied for all three physical* states.[105-7] There is no evidence of any molecular association in the liquid state. Bond energies, bond lengths, and standard thermodynamic quantities have been estimated from the data.[105]

The thermal decomposition of anhydrous perchloric acid has been studied extensively.[108-116] Proceeding through the formation of Cl_2O_7, the following decomposition products are formed at 60-80°; O_2, $HClO_4 \cdot H_2O$, ClO_2, and Cl_2.[111] At 200-439° the products are Cl_2, H_2O, and O_2.[110] In addition to Cl_2O_7, other probable intermediates include ClO_3 and ClO_4. At 10 *mm and 300-400°, the decomposition is first order with re*spect to $HClO_4$. Catalysts, in order of their activity, are $Co_2O_3 > MnO_2 > CuO > Fe_2O_3 > CuCr_2O_4 > Al_2O_3 > SiO_2$.[116]

Reactions

An extremely powerful oxidant, anhydrous perchloric acid causes explosions upon contact with most organic substances. It can, however, be dissolved in chloroform, methylene chloride, acetic acid, and certain other organic solvents for somewhat safer employment in chemical reactions and syntheses. On dissolving it in acetonitrile, it interacts with the solvent by H-bonding initially and then very slowly transfers its proton to the acetonitrile.[117] Applications of the anhydrous acid in various organic solvents have been reviewed by Burton and Praill.[118]

Neither hydrogen chloride nor hydrogen bromide react with anhydrous perchloric acid but hydrogen iodide as well as sodium iodide ignite on contact with it. Thionyl chloride *also ignites on contact but not sulfuryl chloride.* Phosphorous oxychloride dissolves it without reaction, while phosphorous pentachloride reacts to give chlorine heptoxide. A *solution of the acid in chloroform explodes violently if* poured upon phosphorous pentoxide. Reaction with iodine yields deliquescent needles of $HIO_3(I_2\,{}_3$, which when warmed *give off iodine and leave iodic acid as a residue.*

Graphite reacts slowly with the anhydrous acid at room temperature to give $C_{24.9}ClO_4$ and ClO_3.[119] However, a drop *added to wood charcoal* produces a *violent explosion. Paper* and wood are ignited by the acid. The gas-phase reaction of perchloric acid with hydrogen is first order in either reactant and yields hydrogen chloride.[120] Methane or ammonia is without effect on the gas-phase reaction with hydrogen.[121] In the gas-phase reaction of perchloric acid with ethylene the major products are HCl, CO, and H_2O; some 1,2-dichloroethane and vinyl chloride is also produced together with minor amounts of numerous other organic compounds, including C_3 and C_4 halides.[122]

PERCHLORIC ANHYDRIDE

Chlorine heptoxide, the anhydride of perchloric acid, was first isolated by Michael and Conn[30] by adding anhydrous perchloric acid very slowly to phosphorous pentoxide cooled to —10°, and after one day at —10°, distilling the product from the mixture at 82°. They carefully reported that "the apparatus may be virtually pulverized by violent explosion, and personal precautions must be taken accordingly." More recently, Kolarov *et al.*[123] described a method which involves heating a mixture of anhydrous magnesium perchlorate with phosphorous pentoxide in a ratio of 1 to 1-2 at 100-160° and 1-2 mm for 2-5 hours to obtain a pale yellow-to-orange product as distillate collected in a receiver cooled to —78°. The distillate is free of phosphoric acid but contains lower oxides of chlorine. Use of hydrated magnesium perchlorate led to an explosion. Replacement of magnesium perchlorate with potassium or ammonium perchlorate gave no product.

Chlorine heptoxide. Cl_2O_7, is a colorless volatile oil which decomposes spontaneously on standing for a few days, turning greenish-yellow. According to Babaeva,[124] only 33.5% decomposed in 502 min. at 80°. In the presence of 1% $HClO_4$ the rate of oxygen evolution is increased and the final product is oxonium perchlorate.

Perchloric anhydride is soluble in and slowly attacks benzene, reacts slowly with water to form perchloric acid, reacts with iodine to form iodine pentoxide, and explodes on contact with flame or by percussion. It volatilizes rapidly, so that a small amount dropped onto paper or wood may evaporate before it can react violently. Reaction with olefins yields impact-sensitive alykl perchlorates.[125] It is soluble in phosphorous oxychloride, producing normal freezing point lowering indicative of the molecular state Cl_2O_7.[126]

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CHAPTER III

PROPERTIES AND PREPARATION OF PERCHLORATES

REPRESENTATIVE (SUB GROUP A) METAL PERCHLORATES

Ammonium and Alkali Metal Perchlorate

The anhydrous salts of the alkali metal perchlorates are isomorphous with one another and with ammonium, thallium, and silver perchlorates. Their crystal structures have been determined by X-ray and optical methods.[1] With the exception of lithium perchlorate, all exhibit dimorphism undergoing transitions from rhombic to cubic forms at characteristic temperatures.[2-4] Their structural transformations have also been examined by differential thermal analysis.[5,6]

Thermochemical data for various aqueous solutions of the ammonium and alkali metal perchlorates, heats of solution, heats of formation, and thermochemical data for the anhydrous salts have been determined by numerous investigations.[7-12] Solubilities of the perchlorates in various solvents were determined by Willard and Smith.[13] Magnetic susceptibilities[14] and molar refractions[15] have also been determined. Many of the results of these various determinations are compiled in Table 9.

Additional thermochemical data, not included in Table 9 nor in complete agreement with previous data, have been reported recently. Birky and Hepler report heats of solution at 25° for lithium, ammonium and potassium perchlorates of —6.31, 8.02, and 12.31 kcal/mole, respectively.[16] Vorob'ev et al. report that the enthalpies of formation of sodium and potassium perchlorates are —90.68 and —101.9 kcal/mole, respectively.[17]

Guenther[18] found that the solubilities of rubidium and cesium perchlorates in the presence of univalent strong electrolytes (ionic strengths 0.068 to 0.46 *M*) are accurately predicted by simple Debye-Huckel theory. Values obtained for the pKsp (—log of the solubility product) of potassium, rubidium, and cesium perchlorates at 25° are 1.944, 2,542, and 2.380, respectively.

TABLE 9. PHYSICAL PROPERTIES OF AMMONIUM AND ALKALI METAL PERCHLORATES AT 25°C

	Magnitude of Physical Property of Perchlorate					
Physical Property	NH_4	Li	Na	K	Rb	Cs
Density	1.952	2.429	2.499	2.5298	2.9	3.327
Solubility (g/100g solv.)						
Water	24.922	59.71	209.6	2.062	1.338	2.000
Methanol	6.862	182.25	51.36	0.105	0.060	0.093
Ethanol	1.907	151.76	14.71	0.012	0.009	0.011
n-Propanol	0.387	105.00	4.888	0.010	0.006	0.006
Acetone	2.260	136.52	51.745	0.155	0.095	0.150
Ethyl Acetate	0.032	95.12	9.649	0.001	0.016	0.000
Ethyl Ether	0.000	113.72	0.000	0.000	0.000	0.000
Thermochemical data						
ΔH_f°, kcal/mole	—69.42	—91.77	—92.18	—103.6	—103.9	—103.9
ΔF_f°, kcal/mole	....	....	....	—72.7	—73.2	—73.3
ΔS_f°, kcal/mole	....	....	....	36.1	38.4	41.9
C_p°, kcal/mole	....	....	....	26.33	....	25.71
Molar heat of solution	6.36	6.24	3.51	12.1	13.6	13.3
Magnetic subsceptibility (x10^6)	46.3	32.8	37.6	47.4	....	69.9
Molar refraction	17.22	....	13.58	15.37	....	....

Rosolovskii and coworkers[19] report that the solubility of the perchlorates in anhydrous perchloric acid at 0° depends on the radius of the cation but not its nature. The following solubilities (in g of solute per 100 g. $HClO_4$ were found: 0.106 $LiClO_4$, 0.628 $NaClO_4$, 4.256 $KClO_4$, 22.56 $RbClO_4$, and 68.40 $CsClO_4$.

Thermal decomposition and differential thermal analysis studies of the crystalline solids have been carried out by various investigators.[5,6,20-22] Lithium, sodium, and potassium perchlorates yield oxygen and the respective chloride on thermolysis.[20] Gas evolution measurements and DTA[22] indicate that lithium perchlorate melts at 241°, decomposes at 489 , and does not undergo a phase change. By similar means potassium and sodium perchlorates were found to undergo endothermic phase change at 306 and 304°, melt at 575° and 468°, and decompose at 620° and 561°, respectively.[22]

Alkali metal perchlorate solutions have been studied extensively to gain information about the perchlorate ion. From electrical conductance measurements, Jones[23] found a value of 67.32 ± 0.06 mhos for the limiting equivalent conductance of the perchlorate ion. The standard enthalpy of formation of the perchlorate ion in infinitely dilute aqueous solution is —30.87 ± 0.07 kcal/g, according to Kirpichev.[24] The crystal radius of the perchlorate ion is 1.85 Å, determined from results of solvation studies of alkali metal perchlorates.[25] Calculations based on Raman and infrared spectra of aqueous solutions indicate a hydration number of four for perchlorate ions.[26] The tendency for perchlorate ions to form contact ion pairs was studied as a function of cation and solvent by chlorine-35 nuclear magnetic resonance.[27] Factors favoring contact ion pairing are high charge to radius ratio of cation, low dielectric constant of solvent, and low basic strength of solvent. The possibility of perchlorate ion coordination to various metal ions and other species has been explored by vibrational spectroscopy and other techniques and will be discussed in a later section with transition metal perchlorates.

A convenient general preparation method for any alkali metal perchlorate consists of the treatment of the hydroxide, oxide, or metal with perchloric acid followed by isolation of the neutral salt by crystallization. Sodium and potassium perchlorates can be obtained by treating their chlorides or fluorides with nitrosyl perchlorate, $NOClO_4$.[28] Commercial quantities of sodium perchlorate are best prepared by electrolysis of aqueous solutions of sodium chloride.[29,30] Commercial quantities of ammonium, lithium, potassium, rubidium, and cesium are best prepared from sodium perchlorate by metathesis (double-decomposition) reactions, taking advantage of the much higher aqueous solubility of the sodium perchlorate than the other perchlorates in order to fractionally crystallize the desired perchlorate.[29]

Ammonium Perchlorate. The anhydrous salt is prepared by reaction of sodium perchlorate with ammonium sulfate or chloride. No hydrates are known but a triammine with a dissociation pressure of 2 mm at —79° has been reported.[31] Its solubility in ammoniacal solutions increases slightly with increasing ammonia concentration.[32] In aqueous perchloric acid solutions its solubility decreases with increase of perchloric acid concentration and increases with increasing temperature.[33] Densities of aqueous solutions of ammonium perchlorate at 15° and 25° have been determined.[34] An increase in volume results at 25° when ammonium perchlorate is dissolved in water, but a decrease occurs at 15°.

Thermal decomposition of ammonium perchlorate has been studied extensively because of its effectiveness as an oxidant in rocket propellants and as an explosive. It is stable at 110°, decomposes at 130°, and explodes at 380°.[35] Below 300° the decomposition reaction is described by the following equation:[35-38]

$$4\ NH_4ClO_4 \rightarrow 2\ Cl_2 + 8\ H_2O + 2\ N_2O + 3\ O_2$$

Above 400° most of the nitrogen is evolved as nitric oxide.[35] The activation energy for decomposition changes from 18.9 to 29.6 kcal/mole on increasing the temperature above 240°, a change that coincides with the crystal transition from orthorhombic to cubic at 240°. From 400° to 440°, under nitrogen pressure of 20 torr to control sublimation, the decomposition of ammonium perchlorate exhibits an activation energy of 23.4 kcal/mole and probably involves decomposition of the vapor rather than solid phase.[38]

A differential thermal analysis study of the ammonium perchlorate-lithium perchlorate has been reported, indicating a simple eutectic exists at 182° and 69.5 mole % $LiClO_4$.[39] Studies of ternary and quarternary systems involving ammonium perchlorate are cited in the Appendix.

Lithium Perchlorate. The trihydrate is obtained by crystallization from a mixture of lithium carbonate and 70% perchloric acid,[40] or by electrolysis of a solution of lithium chlorate.[41] Conversion of the trihydrate to anhydrous lithium perchlorate, with a molar heat of hydration of 14.2 kcal to overcome, requires prolonged drying at 300°.[40] Pruntsev and coworkers have patented a process for obtaining anhydrous lithium perchlorate by heat treatment at 170-200°.[42]

In addition to forming a very stable hydrate, lithium perchlorate forms a di-, tri-, and pentammine, exhibiting dissociation pressures of 2 mm at 20°, 39.5 mm at 20°, and 31 mm at —79°, respectively.[31]

Lithium perchlorate is thermally stable at and above its melting point at 247°, according to Markowitz.[4] Thermal decomposition, yielding oxygen and lithium chloride, occurs at an appreciable rate at 400° and is catalyzed by the chloride product.[43,44] The autocatalysis is affected by addition of silver nitrate in the lithium perchlorate melt.[44,45]

The solubility of lithium perchlorate in water and the densities of the saturated solutions between 0° and 40° have been determined,[46] also the densities of non-saturated aqueous solutions at 15°.[47] Solubilities in acetone and in methyl ethyl ketone have been reported for the —50° to +50° range.[48]

The structure of lithium perchlorate trihydrate has been determined in detail by an X-ray and neutron diffraction study,[49] and its hydrate water structure has been examined by proton magnetic resonance.[50] The lithium atoms are coordinated by an almost regular octahedron of water molecules (2.133 Å average Li-0 bond distance), the perchlorate ions have a regular tetrahedral structure (1.440 Å Cl-O bond distance), and each hydrogen atom forms a weak bond (2.044 Å) with one perchlorate-oxygen atom and a very weak bond (2.617 Å) with a second perchlorate-oxygen atom.

Sodium Perchlorate. Electrochemical oxidation of aqueous sodium chloride solutions is the most common method for preparing sodium perchlorate. Many different studies, electrodes, and procedures have been described over the years. Improvements recently reported include use of lead dioxide on carbon or titanium as efficient anode materials,[51,52] decreased temperatures,[53,54] and addition of sodium fluoride.[55] For the anodic oxidation of sodium chlorate to sodium perchlorate, increased current efficiency is claimed if potassium persulfate is added.[56] Another approach uses a lead dioxide anode for chlorate concentrations of 250-300 g/l and then changes to a platinum anode when the chlorate concentration has been depleted by electrolysis to one-half its original value.[57]

Sodium perchlorate forms a monohydrate, with a heat of hydration of 2.01 kcal/mole, which can be completely dehydrated at 130°. The anhydrous salt is stable to temperatures up to 471° before loss of oxygen and formation of sodium chloride occurs.[58] Sodium perchlorate also forms a tetrammine.[31]

The solubility of sodium perchlorate in aqueous solutions,[59] perchloric acid solutions,[59] and in water-dimethyl sulfoxide media[60] has been studied. Conductivity of the salt has been measured in water,[61] methanol,[62] ethanol,[63] dimethylformamide,[64] nitromethane,[65] hydrocyanic acid,[66] and hydrazine.[67]

A detailed crystal structure of sodium perchlorate monohydrate has been determined by Berglund and coworkers,[68] who subsequently performed a neutron diffraction study[69] and a deuteron magnetic resonance study of the solid.[70] A chlorine-35 NMR relaxation study of aqueous sodium perchlorate solutions has also been reported.[71]

Studies of ternary and quaternary systems involving sodium perchlorate are cited in the Appendix.

Potassium Perchlorate. The thermal decomposition of potassium perchlorate is complex and has been extensively studied because of the interest in its use as an oxidizer in solid rocket propellants. Decomposition of the pure salt has been detected at a temperature as low as 530°,[72] although others found it to be stable at higher temperatures.[58,73] The kinetics of its isothermal decomposition[74] under constant oxygen pressure[75] and under its own evolved oxygen pressure[76] have been investigated.

No hydrates or ammoniates have been reported for potassium perchlorate. Solubility data up to a temperature of 265° have been determined.[77] Activity coefficients, determined from solubilities in various salt solutions, have been reported.[78] Conductivities in hydrazine,[67] hydrogen cyanide,[66] and dimethylformamide[64] have been measured.

Alkaline Earth Perchlorates

Anhydrous perchlorates of the alkaline earth metals can be prepared by heating ammonium perchlorate with the corresponding oxides or carbonates.[79] They can also be prepared by heating their hydrates with pyridine, eventually driving off pyridine without decomposition of the perchlorate.[80] The hydrates are prepared by treatment of the metal oxides or various salts with aqueous perchloric acid.[13]

All of the alkaline earth perchlorates form hydrates, ammines, and pyridine adducts. The hydrates are identified in Table 10 with data reported for their heats of hydration.[8,81] The ammines correspond to $M(ClO_4)_2 \cdot nNH_3$, where $n = 2$, 6, and 7 for Mg; 2, 3, 4, 6 and 7 for Ca; 1, 2, 6, 7, 10 and 12 for Sr; and 2, 5, 6 and 9 for Ba.[82-84] The pyridine complexes correspond to $M(ClO_4)_2 \cdot n(C_6H_5N)$, where $n = 2$ and 4 for Be; 1, 2, 4 and 6 for Mg; 1 and 2 for Ca and Sr.[80,85] Their thermal stability increases with decreasing number of pyridine groups.

The basic salts $M(OH)ClO_4$ (where M is Mg, Ca, or Ba) have been prepared and characterized.[86]

Alkaline earth perchlorates are unusually soluble in organic solvents, as evidenced by the data of Willard and Smith[13] compiled in Table 10. Curiously, calcium and barium perchlorates are more soluble in methanol than in water. The solubilities of magnesium, strontium, and calcium perchlorates in water have been measured for the 0° to 50° range.[87]

Magnetic susceptibilities[14] and apparent molar volumes,[88] the latter deduced from density measurements of aqueous solutions, are given in Table 10. Vapor pressure[89] and density measurements[90] have also been reported for aqueous solutions of the metal perchlorates at various temperatures.

Beryllium Perchlorate. The dihydrate has been prepared by heating a mixture of beryllium chloride and oxonium perchlorate to 60° in vacuum.[91] Infrared spectra re-

TABLE 10. PHYSICAL PROPERTIES OF ALKALINE EARTH PERCHLORATES AT 25°C

Physical Property	Magnitude of Physical Property of Perchlorate			
	Mg	Ca	Sr	Ba
Solubility (g/100 g Solvent)				
Water	99.601	188.60	309.67	198.33
Methanol	51.838	237.38	212.01	217.06
Ethanol	23.962	166.24	180.66	124.62
n-Propanol	73.400	144.92	140.38	75.65
Acetone	42.888	61.860	150.06	124.67
Ethyl Acetate	70.911	75.623	136.93	112.95
Ethyl Ether	0.291	0.261	0.000	0.000
Heat of formation, ΔH_f°, kcal/mole	—140.6	—178 (est.)	—184 (est.)	—192.8
Heat of hydration, kcal/mole				
Dihydrate	13.509	......	9.5	......
Trihydrate	......	......	......	8.63
Tetrahydrate	24.724	15.485	13.2	......
Hexahydrate	32.708	......	......	......
Apparent molar volume, cm^3/mole	63.2	69.0	71.5	76.3
Magnetic suceptibility ($x10^6$)	65.0	70.5	81.4	94.7
Density of saturated aqueous solution	1.4720	1.7191	2.0837	1.9403

vealed that the product contains $Be(H_2O)_4^{+2}$ and $Be(ClO_4)_4^{-2}$ ions. It melts below 80°, forms an oxo- or hydroxy-containing compound at 150°, loses $HClO_4$ and forms a solid residue $Be_4O(ClO_4)_6$ in the temperature range 190° to 165°, and eventually yields beryllium oxide on further heating to 290°. The tetrahydrate, when heated in an atmosphere of helium, decomposes in the liquid phase to form Be(OH) (ClO_4) which then decomposes to beryllium oxide and anhydrous perchloric acid.[92] Novoselova and coworkers have prepared cesium, rubidium, and potassium perchloratoberyllates of general formula $M_2Be(ClO_4)_4$ and interpreted their infrared spectra obtained as Nujol mulls in the 200-4000 cm^{-1} region.[93]

Magnesium Perchlorate. The anhydrous salt serves as an extremely efficient drying agent.[94] It also strongly absorbs ammonia, ether,[95] and many other polar organic vapors.[96] Vapor pressure measurements have been made of the water-magnesium perchlorate system, indicating the existence of a di-, tetra- and hexahydrate, but no trihydrate.[97]

A thermogravimetric study indicated a gradual weight loss with no sharp break in the temperature-weight curve for magnesium perchlorate hexahydrate decomposing to magnesium oxide.[98] Another study identified $(MgCl)_2O$ as the final product of the thermal decomposition.[99] Markowitz[100] reports that a mixture of magnesium oxide and chloride is formed. A kinetic study by Novoselova and coworkers[101] indicates that magnesium perchlorate undergoes two-stage decomposition: first to $MgO \cdot Mg(ClO_4)_2$, and subsequently to either MgO and $Mg(ClO_4)_2$ (below 165°) or MgO, Cl_2 and O_2 (above 165°).

Conductances have been measured for solutions of magnesium perchlorate in water[102] and various nonaqueous solvents.[103-105] Osmotic and activity coefficients have been reported.[106] The structure of magnesium perchlorate has been investigated by X-ray[107] and Raman[108] techniques.

Calcium Perchlorate. Studies reported for calcium perchlorate include conductivity in acetone,[104] adiabatic compressibility of aqueous solutions,[109] enthalpies of dilution and relative apparent molar enthalpy of aqueous solution,[110] and kinetics of thermal decomposition.[111]

Strontium Perchlorate. Conductances in methanol-acetone solutions[105] and adiabatic compressibility[109] of aqueous solutions of strontium perchlorate have been measured.

Barium Perchlorate. Preparation and use as drying agents of the anhydrous salt[94] and of the trihydrate[112] have been described by Smith. The ammoniates and their equilibrium dissociation pressures have been reported by Smeets.[113] The conductance of barium perchlorate in several different organic solvents has been measured.[114] Vibrational spectra of the crystalline trihydrate have been analyzed,[115] indicating insufficient lattice dissymmetry for a measurable piezoelectric effect or optical activity.

Groups IIIA - VA Metal Perchlorates

Although the perchlorates of all of the representative metals have been prepared, those of Groups III to V of the periodic table have not been studied as thoroughly or as systematically as those of Groups I and II. Perhaps the most distinctive features of metal perchlorates as a class are their relatively large solubilities in organic solvents, their appreciable affinities for water and hydrate formation, and their proclivities to undergo thermal decomposition and sometimes explosions. Most of the literature published on each compound is cited or briefly summarized below.

Aluminum Perchlorate. In addition to the anhydrous salt, five different hydrates have been described with 3, 6, 9, 12 and 15 moles of water.[1] All except the 15-hydrate are hygroscopic. The 9-hydrate has a very high water solubility, 462.75 g per 100 g of water at 0°. Existence of the 12-hydrate has yet to be confirmed. Anhydrous aluminum perchlorate can be prepared by drying its hydrates over phosphorous pentoxide in vacuum at 150°,[116] by treatment of anhydrous aluminum chloride with anhydrous perchloric acid,[117] or by reaction of anhydrous aluminum chloride with silver perchlorate in methanol or benzene.[118]

Viscosities, densities, electrical conductances, molar refractions, molar volumes, and compressibilities of various aqueous solutions of aluminum perchlorate have been reported.[119-122] Conductivities have also been determined in some nonaqueous solvents.[117,123] Thermal decomposition studies have been made identifying aluminum oxide as the final product.[20,124] Vibrational spectra indicate that the anhydrous compound is covalent with bidentate perchlorate groups.[125] Raman spectra of aqueous solutions[126] and proton magnetic resonance spectra of alcoholic solutions[127] have been analyzed.

Preparation of perchloratoaluminates, with infrared spectra indicating a general structure $M[Al(ClO_4)_4(H_2O)_2]$ (where M is either cesium or rubidium), has been reported.[128] Tetraalkylammonium haloperchloratoaluminates have also been prepared.[129]

Gallium and Indium Perchlorates. Viscosities and densities of aqueous solutions of gallium and indium perchlorate have been measured over the temperature range 18° to 90°.[122] Sound velocities and densities also have been determined at 25°.[121] Gallium perchlorate is very deliquescent, highly soluble in water, forms a 6- and a 9-hydrate, and decomposes at 155° in a vacuum or at 175° exposed to air. Attempts to dehydrate the hexahydrate produced a basic salt. Isospiestic studies of aqueous solutions of gallium perchlorate have been made,[130] and activity coefficients have been measured.[131] Indium perchlorate has been little studied.

Thallium Perchlorate. The crystal structure of thallium perchlorate is isomorphous with the alkali metal perchlorates, except for the lithium salt. Conductivity measurements indicate a dissociation constant of 1.00 in water at 25°.[133] Activity coefficients[132] and sedimentation equilibria[134] have been determined. Density and refractive indices of the solid have been measurd.[135] The solid is volatile at low pressures at 200°,[136] undergoes an orthorhombic-cubic transition at 285°, and decomposes above 430° (with an activation energy of 54 kcal/mole) to yield Tl_2O_3 and TlCl (relative amounts depend on both temperature and atmospheric composition).[136,137]

Group IVA Metal Perchlorates. Preparation of either germanium or tin perchlorate has not been reported. Lead perchlorate has been prepared in anhydrous form and as the mono- and tri-hydrate.[138] It is extremely soluble in water, forming a saturated solution at 27° with a density of 2.7753. Use of aqueous solutions of lead perchlorate has been suggested for determining densities of insoluble solids by the suspension method.[139] An anhydrous solution of lead perchlorate in methanol is explosive. Basic salts have been prepared by reaction of lead oxide with perchloric acid.[140] Perchlorato complexes of lead have been prepared also,[141] providing the earliest evidence that perchlorate ions can coordinate to metal ions.

Group VA Metal Perchlorates. Antimony oxyperchlorate pentahydrate has been obtained in crystalline form by cooling a solution of freshly precipitated $Sb(OH)_3$ dissolved in warm 70% perchloric acid.[142] The solid compound decomposes above 60° to antimony oxides, and it is dissolved but hydrolyzed by water.

Bismuth perchlorate is prepared as the pentahydrate by reaction of bismuth oxide and perchloric acid.[142] Preparation from metallic bismuth and perchloric acid generally leads to an explosion.[142,143] Bismuth oxyperchlorate can be obtained by hydrolysis of bismuth perchlorate in 40% perchloric acid. Raman spectra have been determined for both $Bi(ClO_4)_3$ and $BiOClO_4$.[126] The crystal and molecular structure of u-oxo-bis(perchloratotriphenylbismuth) have been investigated, indicating that the perchlorate groups are weakly coordinated to bismuth(V).[144]

TRANSITION METAL PERCHLORATES

Much of the interest surrounding the preparation and study of transition metal perchlorates seems to have been focused on three questions: (1) how does the nature of the metal cation influence thermal decomposition of perchlorates?, (2) can advantage be taken of the solubility of metal perchlorates in various solvents to effect separation or other applications?, and (3) to what extent will perchlorate ions coordinate to metal ions? Other than this, the transition metal perchlorates have been explored relatively little. More attention has been given to the solution chemistry of the transition metal ions in the presence of perchloric acid or perchlorates than to the properties of the metal perchlorates.

The crystal structures of the hexahydrates of a number of bivalent metal perchlorates have been determined.[107]

Hexagonal structures, closely related to that of lithium perchlorate trihydrate, are exhibited by the manganese, iron, cobalt, nickel, zinc, and cadmium compounds. Mercuric perchlorate hexahydrate is trigonal, and cupric perchlorate hexahydrate is monoclinic. Infrared spectra of some fully hydrated transition metal perchlorates indicate that the perchlorate group exists in the solids as simple perchlorate ions. For certain lower hydrates, the spectra suggest the presence of coordinated perchlorate groups.[145]

Solubilities in water and other polar solvents are generally appreciable for most metal perchlorates, as exemplified by the data compiled in Table 11. Conductivities and other electrochemical properties of some of the perchlorates in furfural and in Cellosolve have also been reported.[114] Viscosities, densities ,and electrical conductances of 0.001-2 M aqueous solutions of chromium(III), iron(II), thorium(IV), and silver(I) perchlorates at 20°-35° have been determined, also molar refractions and apparent molar volumes of the salts.[120]

A general method of preparing transition metal perchlorates in solution has been described which consists of three main steps: (1) dissolution of a weighed amount of the metal in azeotropic hydroiodic acid, (2) addition of the requisite weighed amount of standard perchloric acid, and (3) removal of the hydroiodic acid by oxidation with ozone followed by volatilization of the iodine formed.[146] In some cases, the simple expendient of dissolving the metal or its hydroxide, oxide, or carbonate is satisfactory. Preparation of the pure solids is frequently complicated by the tendency of the transition metal ions to undergo hydrolysis, yielding hydroxyperchlorates.

Pyridine complexes of a number of bivalent metal perchlorates and silver perchlorate have been prepared and characterized.[85] Hydroxyperchlorates of zinc, cadmium, mercury, and copper have been prepared by dissolving the oxides in solutions of the corresponding perchlorates.[147]

Thermal decomposition studies of some first-row transition metal perchlorates have been carried out by DTA and TGA techniques.[148,149] Stabilities decrease with increasing effective electrical field strength of the metal ion. Activation energies found for the decomposition of $Mn(ClO_4)_3 \cdot 6\,H_2O$,

TABLE 11. SOLUBILITY OF METAL PERCHLORATES[114]

Salt	Solubility (g solute/100 ml solvent) in Solvent		
	Water	*Furfural*	*Cellosolve*
$Ba(ClO_4)_2$	—	50	100+
$Cd(ClO_4)_2 \cdot 6H_2O$	478	80	145
$Cu(ClO_4)_2 \cdot 6H_2O$	—	70	100+
$Cu(ClO_4)_2 \cdot 2H_2O$	259	20+	—
$Co(ClO_4)_2 \cdot 6H_2O$	292	60	110
$Mn(ClO_4)_2 \cdot 6H_2O$	268	90	130
$Ni(ClO_4)_2 \cdot 6H_2O$	267	60	100+
$Ni(ClO_4)_2 \cdot 2H_2O$	—	20	35
$AgClO_4$	540	40	125
$Pb(ClO_4)_2$	—	25	105
$Zn(ClO_4)_2 \cdot 6H_2O$	—	85	130

$Co(ClO_4)_3 \cdot 3H_2O$, $Ni(ClO_4)_2 \cdot 6H_2O$, and $Cu(ClO_4)_2 \cdot 6H_2O$ are respectively 21.4, 24.8, 49.0-52.0, and 43.7-45.9 kcal/mole.[149] The hexahydrate of chromic perchlorate undergoes simultaneous dehydration and decomposition to chromic oxide without forming anhydrous chromic perchlorate, and the dihydrate decomposes at 135°-160° with an energy of activation of 17.5 kcal/mole.[150] Bel'kova and coworkers have investigated the thermal behavior of many of the rare earth perchlorates, including determination of their dehydration and thermal decomposition temperatures.[151-153] At 500° all the perchlorates decomposed similarly to give both MOCl and MCl_3 in the solid residue. Thermograms show endothermic effects due to loss of water of crystallization followed by exothermic effects accompanying decomposition of the perchlorate. Most of the hydrated perchlorates lose water gradually up to 200° and begin decomposition in the temperature range 250°-270°. Thermal decomposition is facilitated with increasing polarization effects of the cation. For the trivalent rare earth perchlorates, in the series lanthanum through holmium, increasing atomic number (decreasing cation radius) is accompanied by a decrease in the decomposition temperature.[151] Thermogravimetric studies of the lanthanide perchlorates indicate that dehydration is affected more than the decomposition process by change in applied pressure.[154] Decomposition under non-isothermal conditions yields chlorides. To obtain anhydrous perchlorates it is best to operate at very low pressure and slow heating rates to minimize formation of oxychlorides.

The perchlorate ion was long considered to be a noncoordinating anion and thus ideally suited for avoiding competitive complexation and for maintaining a constant ionic medium in complex equilibria studies. However, findings reported in the early 1960's[145,155,156] and the many investigations that followed have proved this conception false. Vibrational spectroscopy and single crystal X-ray diffraction techniques provided the most convincing evidence of perchlorate coordination. In the absence of strongly coordinating solvent molecules or other ligands, transition metal ions are particularly receptive to perchlorate ion association and complexation. Examples include the ions of chromium,[157] manganese,[158] iron,[159] cobalt,[158-161] nickel,[158-161] copper,[158-163] zinc,[158,159] mercury,[159] cerium,[159] and thallium.[159] Although quantitative data are lacking in most cases, the perchlorato complexes of metal ions are invariably weak. Labile aquated metal ions are much less prone than inert complex metal ions to form perchlorato complexes of measureable stability. The role of the perchlorate ion as a ligand in solution and the myth of non-coordinating anions have been the subject of recent review articles.[159,164]

Group IB and IIB Metal Perchlorates

Copper and silver perchlorates have been investigated rather extensively, but no studies have been reported of gold perchlorate. Heats of formation of cupric and silver perchlorates in aqueous solutions are —19.0 and —7.75 kcal/mole, respectively. Cupric perchlorate is prepared by dissolving basic copper carbonate in perchloric acid. Its most stable hydrated form is the hexahydrate, which has a m.p. of 82.3°, a water solubility at 23° of 54.3% (density 2.225 g/ml), and a molar heat of solution of —4.6 kcal. Hepta-, tetra-, and di-hydrates have also been described.[131] Silver perchlorate is obtained as a monohydrate on crystallization from aqueous solution and easily converted to the anhydrous form on drying at or above 43°. It is deliquescent, explosive, light sensitive, and very soluble in water. At 0° a saturated aqueous solution of silver perchlorate contains 82.07% $AgClO_4$ and has a density of 2.7251; at 35° it contains 86.21% $AgClO_4$ and has a density of 2.9173.

Silver perchlorate has been reported to explode on pulverizing it in a mortar. In spite of its hazards, silver perchlorate has received considerable attention because of its unusual solubility in organic solvents and ability to form certain addition compounds. It can be used to generate anhydrous perchloric acid in various organic solvents by bubbling dry hydrogen chloride through its solution in the respective solvent. Its solubility in grams per 100 grams of solvent at 25° is 5.28 in benzene, 101 in toluene, 5.28 in aniline, and 26.4 in pyridine. It is also soluble in nitrobenzene, chlorobenzene, glycerine, glacial acetic acid, acetonitrile, nitromethane, and ethyl acetate. It is insoluble in chloroform, carbon tetrachloride, and ligroin. Silver perchlorate is appreciably associated in many solvents.[62,63,114,167] In aprotic solvents of dielectric constant greater than 30 it behaves as a medium-strength electrolyte.[168] In anhydrous hydrofluoric acid, hydrocyanic acid, or polar solvents of high dielectric constant it is extensively ionized. Silver perchlorate has proven useful as a reagent in organic synthesis, as described in Chapter V.

Studies on zinc perchlorate include determination of water vapor pressure of aqueous solutions (0.5 *M* to saturated) at 0° and 50°,[169] measurement of conductances in the mixed solvent methanol-acetone,[105] determination of osmotic and activity coefficients,[106,170] and measurement of heats of dilution with water and with perchloric acid.[171]

Cell potential measurements indicate that zinc and cadmium perchlorates are completely dissociated in concentrations up to 0.1 *M* in aqueous solution (in contrast to the non-dissociated halides) and that the mean transport number of the perchlorate ion is 0.595.[172,173] Both zinc and cadmium perchlorates form tetra- and hexa-ammoniates.[174] The dissociation pressure and composition of the zinc compound have been determined as a function of temperature and its heat of formation calculated.[82,175]

Mercurous perchlorate forms a tetrahydrate which can be readily converted to the dihydrate on heating above 36°.[176] In water it can undergo three successive stages of hydrolysis, eventually yielding mercurous oxide. Conductance and potentiometric measurements of highly concentrated solutions indicate abnormal dissociation. Mercury(I) is reported to form a stronger perchlorato complex than mercury(II).[177]

Group IIIB and Rare Earth Metal Perchlorates

Aqueous solutions of scandium, yttrium, and lanthanum perchlorates have been investigated by viscosity and density measurements over the temperature range 25° to 90°. Results indicate that hydration of the cation is weaker the larger its radius.[178] Apparent molar volumes, specific adiabatic and molar compressibilities, and isobaric and molal expansions have also been determined as a function of concentration.[179]

Spedding and coworkers have conducted numerous, extensive investigations of aqueous solutions of rare earth perchlorates. Results reported include densities, equivalent conductances, transference numbers,[180] activity coefficents,[180,181] heats of dilution at 25°,[182] and partial molal heat capacities at 25°.[183]

The solubilities of the lanthanide group metal perchlorates have been determined over the temperature range 25° to 50°. They show very little temperature dependence.[184] Heats of solution of the tetrahydrates in water have been determined also.[185]

Ammoniates[186] and antipyrine complexes[187] of some of the lanthanide group metal perchlorates have been prepared and described. Thermal decomposition of the ammoniates proceeds through several steps, yielding the metal chlorides at 500°.[186]

Neodymium perchlorate hexahydrate has been prepared and dried at 170° to yield the anhydrous solid.[187] Its molar refraction and absorption spectrum in aqueous solution have been determined.[188] Gadolinium perchlorate octahydrate also has been prepared. It is deliquescent and very soluble in water and in alcohol.[189,190]

Several rare earth perchlorates of the actinide group have been prepared: solid uranyl perchlorate,[191] solutions of neptunium(IV), (V), and (VI) perchlorates,[192] and plutonium(III) perchlorate.[193]

Group IVB - VIIB Metal Perchlorates

Preparations of perchlorates of only the first member of each group have been reported. Titanium tetraperchlorate sublimes at 70°, decomposes on aging at 70° in a vacuum, and explodes when heated at atmospheric pressure to about 130°.[194] Anhydrous titanium tetraperchlorate and chromyl perchlorate reportedly contain bidentate perchlorato ligands.[195] Vanadyl perchlorate pentahydrate, $VO(ClO_4)_2 \cdot 5H_2O$, has been prepared by dissolving vanadium(IV) hydroxide in perchloric acid followed by precipitation from 3.5 M perchloric acid.[196] On heating to 140° it loses one water of hydration and is partially oxidized to vanadium(V), at 200° loss of $HClO_4$ occurs, and at 300° formation of vanadium pentoxide takes place exothermically. Absorption spectra of solutions of vanadium(III) and vanadium(IV) perchlorates have been determined.[197] Chromic perchlorate has been prepared in hydrate form containing 3, 5, 6, 9, and 10 moles of water.[198] Manganese perchlorate hexahydrate is deliquescent, melts at 155°, begins thermal decomposition at 165°, and decomposes rapidly at 230° to manganese dioxide. Its anhydrous salt could not be prepared in pure state.[199] Results of an electron paramagnetic resonance study of manganese(II) in aqueous perchloric acid solutions at 25° and 55° have been interpreted to indicate the presence of an internal monoperchlorato complex, with a stability constant of $(8.0 \pm 1.5) \times 10^{-2}$.[200]

Group VIIIB Metal Perchlorates

Ferrous perchlorate hexahydrate forms long green crystals, is stable in air, loses four molecules of water over 96% sulfuric acid in a vacuum, and is susceptible to air oxidation in aqueous solution.[201] Its solubility in water is 978 g/l at 0° and 1161 g/l at 60°. In ethanol at 20° its solubility is 865.4 g/l. Ferric perchlorate decahydrate loses four molecules of water over concentrated sulfric or phosphorous pentoxide. It is soluble in water to the extent of 1198 g/l at 0° and 1517 g/l at 60°. The existence of perchlorato complexes of iron(III) has received considerable attention by many investigators. Johansson, after a critical review of the literature, concluded that more experimental work of high quality is necessary to settle the issue.[159]

Cobalt(II) and cobalt(III) perchlorates have been prepared, the latter by electrolytic or fluorine oxidation of the former.[202] Anhydrous cobalt(II) and nickel(II) perchlorates reportedly can be prepared either by heating the corresponding hexahydrates below their melting points in a vacuum or by first replacing their water of hydration with dimethoxypropane and then vacuum heating.[203] Hexapyridine complexes of cobalt(II) and nickel(II) perchlorates can be prepared by reaction of the respective perchlorate with pyridine.[85]

Rhodium(III) perchlorate hexahydrate forms light yellow, long needles, is hygroscopic, and has a face-centered cubic structure.[204] Rhodium(IV) perchlorate is dark red and has been prepared only in solution, by dissolving $RhO_2 \cdot 2H_2O$ (obtained as a precipitate by oxidizing $RhCl_3$ in alkaline solution with sodium hypobromite) in 1 *M* perchloric acid.[205] Palladium(II) perchlorate tetrahydrate has been prepared by *dissolving palladium sponge in concentrated nitric acid* followed by heating to fumes with 72% perchloric acid.[206] The brown crystalline needles deliquesce in moist air but can be dried over phosphorous pentoxide in a vacuum without loss of the hydrate water.

MISCELLANEOUS PERCHLORATES

Inorganic Perchlorates

Certain non-metallic elements and compounds, notably those of nitrogen, phosphorous and the halogens, enter into chemical combination with perchloric acid and its derivatives to provide a number of interesting inorganic compounds. These are briefly reviewed below.

Nitronium Perchlorate. This compound, also called nitryl or nitroxyl perchlorate, was first prepared by Gordon and Spinks[207] in1940 by mixing chlorine dioxide with a mixture of ozone and nitrogen oxides generated by passage of dry air through an ozonizer. It has also been prepared by reaction of dinitrogen pentoxide with anhydrous perchloric acid.[208] Nitronium perchlorate is composed of NO_2^+ and ClO_4^- ions,[209] has a very low vapor pressure, is soluble in and recrystallizable from nitric acid, and reacts very rapidly with water to give nitric and perchloric acids with moderate evolution of heat. It reacts vigorously with many organic compounds, explosively with some. Solutions of NO_2ClO_4 in nitromethane or chloroform have been used to nitrate aromatic compounds. Raman spectra of crystalline nitronium perchlorate[210] and of its nitric acid solution[211] have been reported. *Thermal decomposition at 100-127° yields, among* other products nitrosyl perchlorate.[212] Reaction with metal oxide yields the metal perchlorate.

Nitrosyl Perchlorate. Raman spectroscopy indicates that the compound $NOClO_4$ is composed of NO^+ and ClO_4^- ions.[213] It has an orthorhombic crystal structure,[214] a density of 2.169 g/cc,[215] and a heat of formation of —41.79 ± 0.08 kcal/mole.[216,217] Reaction with water produces nitrogen oxides. With methanol, nitromethane is formed. Nitrosyl perchlorate reacts violently with many organic compounds. It was first prepared by passing a mixture of nitric oxide and nitrogen dioxide into 72% perchloric acid followed by fuming to 140° and cooling to crystallize out the monohydrate.[218] The anhydrous salt was obtained on drying over phosphorous pentoxide, first in an atmosphere of nitrogen oxides and then in a vacuum. Its thermal decomposition has been studied extensively, and nitronium perchlorate is one of the products.[219,220]

Hydrazine Perchlorate. The hemihydrate, $N_2H_5Cl_4$ $\frac{1}{2}H_2O$, is obtained on neutralization of an aqueous solution of hydrazine with perchloric acid. At or below 60.5° the equilibrium dissociation pressure of the hydrate follows the equation[221]

$$\log P_{mm} = -3047.6/T + 10.98$$

The free energy of dehydration is 1.456 kcal/mole, and the heat of dissociation is 13.95 kcal/mole. The anhydrous salt can be readily recrystallized from ethanol, with a solubility at 60° of 69 g/100g solution and at 0° very slight.[222] It melts at 137-8° and begins to decompose at 145°. Deflagration results if it is heated rapidly. Violent detonation occurs on mechanical impact, shock, or friction.[223]

Phosphonium Perchlorate. A crystalline product, m.p. 46-47°, formulated as $P(OH)_4ClO_4$, has been obtained through the interaction of phosphoric and perchloric acids. Soluble in nitromethane, its conductivity is typical of an ionic salt. Heats of solution and formation in nitromethane are 13.9 and 11.4 kcal/mole, respectively.[224,225]

Selenious Acid Salt. Addition of selenious acid to ice-cold perchloric acid, after warming slightly and then cooling again, yields a crystalline, deliquesent product of formula $Se(OH)_4ClO_4$. In nitromethane, its heats of solution and formation are 4.8 and 11.4 kcal/mole, respectively, and conductivity measurements are indicative of an ionic salt.[225]

Perchloryl Fluoride. The compound ClO_3F undergoes a number of interesting and useful reactions: at 150 to 300° it vigorously oxidizes a variety of reducing agents, with ammonia it forms ammonium perchlorylamide, with aromatic compounds it forms perchloryl substituted compounds, and for certain active hydrogen containing compounds it is an effective fluorinating reagent.[226] Surprisingly stable, perchloryl fluoride can be heated in glass to the softening point without etching the surface. Treatment with a concentrated strong base or heating with water at 250 to 300° in a sealed tube is necessary for quantitative hydrolysis to fluoride and perchlorate ions.[227]

Perchloryl fluoride has been prepared by the action of fluorine on potassium chlorate,[228] by electrolylsis of sodium perchlorate in liquid hydrogen fluoride,[229] and by the action *of fluorosulfonic acid on perchlorates.*[230] *Its physical* properties have been studied extensively; values reported for some constants include: m.p. —146°, b.p. —46.8°, heat of vaporization 4.6 kcal/mole, critical temperature 95.13°, critical pressure 53.00 atm, critical density 0.637 g/cc, critical molar volume 161 cc, dipole moment 0.023 ± 0.003D, and $\Delta H^{\circ}_{f\ 298} = -5.12 \pm 0.68$ kcal/mole.[227,231,232] Thermodynamic properties,[226,233] vapor pressure,[231] surface tension,[232] and viscosity[232] have been measured over various temperature ranges.

The infrared spectrum and fundamental vibration frequencies of perchloryl fluoride have been determined.[227,234,235] The fluorine and three oxygen atoms are bonded separately to the chlorine atom.

Halogen Perchlorates. Fluorine perchlorate, m.p. —167.5 and b.p. —167.5°, has been prepared by reaction of elemental fluorine with 60 to 72% perchloric acid.[236] It is reported to explode always on freezing or when contacted with organic or easily oxidized matter. Chlorine perchlorate, $ClOClO_3$, has been prepared by the reaction at —196° of $ClSO_3F$ with cesium perchlorate or nitrosyl perchlorate.[236] *Bromine perchlorate (red liquid, f.p. < —78°) was prepared* from the chlorine perchlorate (pale yellow liquid) by treatment with bromine at —35 to —78°.[236] Both halogen perchlorates react at —78° with anhydrous metal chlorides to form metal perchlorates and with gaseous hydrogen chloride or bromide to yield anhydrous perchloric acid and the respective halogen. They also react with fluorocarbon halides to yield novel fluorocarbon perchlorates[237] and with perhaloolefins to form perhaloalkyl perchlorates.[238]

Iodine trisperchlorate has been obtained as a white solid in excellent yield by treating iodine with chlorine perchlorate at —150° for 70 hours.[239,240]

Organic Perchlorates

Innumerable perchlorate salts of organic bases and chelated metal cations have been reported. Most were prepared as a convenient means of isolating the desired base or cation in a crystalline form of definite chemical composition. Few have been prepared for the purpose of investigating perchlorate chemistry. All show typical perchlorate properties: moderate to good solubility in organic solvents, relatively high conductivity, tendency to decompose at or above their melting point, and the capability of explosive behavior if overheated or detonated by mechanical shock. Representatives of this group are the perchlorates of methylamine,[241] pyridine,[242] benzenediazonium ion,[743] and bis(1,10-phenanthroline)copper(I) ion.[244] Except for the diazonium perchlorates, which are extremely explosive and easily detonated, most perchlorate salts can be handled safely with suitable care.

Aromatic aldehydes, ketones, ethers, and various pyran compounds combine with perchloric acid to form crystalline salts that can be isolated, although they often decompose on storing.[245] Some controversy exists as to whether certain of these should be considered as oxonium or carbonium salts. True carbonium salts, identifiable by their conductivity in nonaqueous solvents and intense color, are formed by the action of perchloric acid on triarylmethylcarbinols or by metathesis of the cloride with silver perchlorate in a suitable solvent.[246,247]

Preparation of the gem-diperchlorate $(CH_3)_2C(OClO_3)_2$ from acetone has been reported, also the gem-diperchlorate of 2-butanone.[248] Alkyl diperchlorates have been prepared from dienes and diols.[249]

Relatively few perchloric esters have been isolated or their physical properties determined because of the severe explosion hazard involved. Meyer and Spormann[250] reported that the methyl ester (b.p. 52°) and the ethyl ester (b.p. 89°) are extremely powerful explosives and that they were unable to avoid explosions in spite of great foresight taken in handling them. Ethyl perchlorate, first prepared by Hare and

Boye in 1841,[251] is immiscible with water and slowly hydrolyzed by it. It is soluble in ethanol but still dangerous to handle, because a dilute solution can spontaneously burn completely away if not explode. Preparations reported for other perchlorate esters include those for $ClCH_3CH(OH)CH_2ClO_4$,[252] $HOC_2H_4OC_2H_4ClO_4$,[252] trichloromethyl perchlorate,[253,254] acetyl perchlorate,[255] and benzoyl perchlorate.[255]

Perchloryl compounds can be prepared by reaction of perchloryl fluoride with aromatic compounds in the presence of anhydrous aluminum chloride.[256] For example, perchloryl benzene ($C_6H_5ClO_3$, mp.m.△3°, b.p. 232°) has been obtained by this Friedel-Crafts type reaction. It is reasonably stable. Hyrolysis with potassium hydroxide solution produces potassium chlorate and phenol, and nitration with a mixture of concentrated sulfuric and nitric acid yields 3-nitroperchlorylbenzene (pale yellow needles, m.p. 49 to 50°). The relative stability of the perchloryl group towards reductants is evidenced by its ability to remain intact when 3-nitroperchlorylbenzene is reduced with stannous chloride in hydrochloric acid to 3-aminoperchlorylbenzene.[256] Although relatively safe to prepare and use, perchloryl aromatic compounds are sensitive to vigorous shock and high temperature.

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CHAPTER IV

APPLICATIONS OF PERCHLORIC ACID AND PERCHLORATES IN CHEMICAL ANALYSIS

DISSOLUTION AND OXIDATION OF INORGANIC SAMPLES

Perchloric acid, alone or in combination with other strong mineral acids, is frequently employed to dissolve or decompose inorganic substances as an integral step in their analysis. In most instances the dissolution process is more efficient than if some other acid were to be used. Often more suitable oxidation states of the sought-for substances are attained which facilitate or make possible their subsequent separation or determination. Moreover, if silica is present its determination can be greatly simplified by the strong dehydrating action of hot, concentrated perchloric acid.

In the process of decomposing samles with hot acid, especially when prolonged heating or evaporation to dryness is involved, it is important to be aware of the possibility of loss of certain elements by volatilization. Obviously, one should guard against unintentional loss of sought-for substances. A second consideration is the possibility that separations can be achieved if sufficient differences in volatility exist. The necessary information for such considerations in the case of perchloric acid treatment of inorganic samples is available from comprehensive studies by Hoffman and Lundell[1] and by Chapman and coworkers.[2] Their results are compiled in Tables 12 and 13, respectively. Among the many conclusions that can be draw from these results, the following are illustrative: (1) chromium can be satsifactorily separated from manganese in analyses of steels containing high percentages of chromium, (2) rhenium can be separated from molybdenum by distillation from a mixture of perchloric and phosphoric acids to which hydrobromic acid is slowly added, and (3) boron can be quantitatively distilled from perchloric and hydrofluoric acid mixtures.

Soils, Clays, and Silicates

A number of successful procedures have been described for the analysis of soil, clays, and silicates based upon the

TABLE 12. ELEMENTS AND APPROXIMATE PERCENTAGES VOLATILIZED[a]

Elements	Acid Mixture Distilled at 200-220°					
	HCl $HClO_4$	HBr $HClO_4$	HCl-H_3PO_4 $HClO_4$	HBr-H_3PO_4 $HClO_4$	HCl H_2SO_4	HBr H_2SO_4
Alkali metals	0	0	0	0	0	0
Alkaline earth metals	0	0	0	0	0	0
Rare earth	0	0	0	0	0	0
Group III elements	0	0	0	0	0	0
Cu, Ag, Zn, Cd	0	0	0	0	0	0
Al, Ga, In	0	0	0	0	0	0
Ti, Zr, Hf, Si, Pb	0	0	0	0	0	0
Nb, Ta, W	0	0	0	0	0	0
Fe, Co, Ni	0	0	0	0	0	0
Rh, Pd, Ir, Pt	0	0	0	0	0	0
As(III)	30	100	30	100	100	100
As(V)	5	100	5	100	5	100
Au	1	0.5	0.5	0.5	0.5	0.5
B	20	20	10	10	50	10
Bi	0.1	1	0	1	0	1
Cr(III)	99.7	40	99.8	40	0	0
Ge[b]	50	70	10	90	90	95
Hg	75	75	75	75	75	90
Mn	0.1	0.02	0.02	0.02	0.02	0.02
Mo	3	12	0	0	5	4
Os[c]	100	100	100	100	0	0
P	1	1	1	1	1	1
Re	100	100	80	100	90	100
Ru	99.5	100	100	100	0	0
Sb	2	99.8	2	99.8	33	99.8
Se	4	5	5	5	20	100
Sn(II)	99.8	100	0	99.8	1	100
Sn(IV)	100	100	0	100	30	100
Te	0.1	0.5	0.1	1	0.1	10
Tl	1	1	1	1	0.1	1
V	0.5	2	0	0	0	0

[a] Results of Hoffman and Lundell[1] obtained by treatment of the elements or their salts with 15 ml of 60% perchloric acid (or sulfuric acid), maintained at 200-220° and purged moderately with a stream of dry carbon dioxide, while slowly adding 15 ml of hydrochloric or hydrobromic acid. The same procedure was used for distillations from phosphoric acid mixtures except 5 ml of sirupy phosphoric acid was added to the 15 ml of 60% perchloric acid prior to heating and further treatment.

[b] To prevent precipitation of GeO_2, the hydrochloric or hydrobromic acid was added before heating the final solution.

[c] At 200 to 220° no osmium was volatilized from the sulfuric acid solutions; however, at 270 to 300° the osmium was completely volatilized.

TABLE 13. EFFECT OF TREATMENT WITH PERCHLORIC AND HYDROFLUORIC ACIDS[a]

Elements Retained	Elements Lost
Na, K	B, 100%
Cu, Ag, Au	Si, 100%
Be, Mg, Ca, Sr, Ba	Ge, up to 10%
Zn, Cd, Hg	As, 100%
La, Ce	Sb, up to 10%
Ti, Th	Cr, varies greatly
Sn, Pb	Se, varies greatly
V, Bi	Mn, up to 3%
Mo, W, U	Re, varies greatly
Fe, Co, Ni	

[a] Results of Chapman and coworkers[2] obtained by fuming a solution of the element or its compound with a mixture of 10 to 15 ml of 70% perchloric acid and 8 to 10 ml of hydrofluoric acid in a platinum dish at approximately 200°.

use of perchloric acid to decompose the sample. Among the first to advocate the use of perchloric acid in cehmical analysis, Willard and Cake[3] found it to be ideally suited for the determination of silica in silicates due to the strong dehydrating action provided by boiling the concentrated perchloric acid solution. Cadariu recommended perchloric acid for the analysis of silicon in silicates[4] and for use in decomposing slags, dried cement slurries, Portland cement, bauxite, and clay.[5] Marczenko and Stepien[6] found perchloric acid to be superior to hydrochloric or sulfuric acid for the determination of silica in aluminosilicates. Turek[7] employed mixed hydrofluoric and perchloric acids for the decomposition of clay samples. Pratt[8] described a similar treatment for soils to be analyzed for total potassium and sodium.

The determination of nitrogen and phosphorous in soils can be effected rapidly through the use of decomposition with perchloric and sulfuric acid according to Meshcheryakov.[9] Sommers and Nelson[10] employed perchloric acid digestion in a sealed tube to achieve rapid and precise determination of phosphorous in a wide range of soils. Metson and Collie[11] have proposed the use of nitric, perchloric, and phosphoric acids for the determination of total sulfur in soils. Potassium content of soils have been estimated by a perchloric acid extraction method.[12]

Metals, Alloys and Ores

Chemical analysis of steels has been greatly facilitated by use of perchloric acid to dissolve the samples, dehydrate the silica, and oxidize chromium and certain other constituents to oxidation states that enable their simple and direct determination. Willard and Cake[3] were the first to describe the use of perchloric acid for the determination of silica in steel. They were also first in determining chromium in steel employing hot, concentrated perchloric acid to oxidize the chromium to dichromate.[13] Another first by Willard in analytical applications of perchloric acid was its use for the determination of vandium as well as chromium in steel, chromite, and ferrochromium.[14] Perchloric acid soon became the acid of choice for steel analysis, with many advocating its use and reporting extensions and refinements of Willard's methods. Smith and Smith[15] demonstrated that a mixture of perchloric and phosphoric acids rapidly and completely dissolves chromium steel, stainless steel, tungsten steels, and metallic tungsten. Seuthe and Schaefer[16] employed a mixture of perchloric and nitric acids to dissolve steel in analysis for chromium, vanadium, tungsten, and phosphorous. Rapid determination of silicon, chromium, nickel, and molybdenum in steel and copper alloys was reported by Birckel.[17] Use of perchloric acid for analysis of steels, alloyed cast iron, and other materials was described by Raab,[18] Croall,[19] and Bertiaux and coworkers.[20] The determination of chromium in steel by oxidation with perchloric acid has been investigated by various workers to find optimum conditions.[21,22] More recently, spectrophotometric methods for the determination of manganese,[23] chromium and manganese,[24] and zirconium[25] have been reported for the analysis of iron and steels following treatment with perchloric acid.

Methods utilizing mixtures of perchloric, phosphoric, and sulfuric acids for the determination of manganese in tungsten and ferrotungsten,[26] for the determination of chromium in chromite ores,[27] and for the analysis of ferrochrome[28] have been published by Smith and coworkers.

Iron ore samples are rapidly and completely dissolved by an equal volume mixture of 72% perchloric acid and 85% phosphoric acid. Goetz and Wadsworth[29] reported that nearly all iron ores are dissolved within 10 minutes and the determination of iron can be accomplished without difficulty by passing the perchloric acid solution through a Jones reductor and titrating with standard cerium(IV) sulfate or potassium permanganate.

Analysis of chromium metal for lead following preliminary dissolution and oxidation with perchloric acid has been reported.[30] A method for the determination of iron and cobalt in stellite (a nonferrous alloy of Cr, W, Co, and C) has been described[31] based upon the use of perchloric acid oxidation and distillation of chromium as chromyl chloride to eliminate interference by chromium.

Miscellaneous Samples

Perchloric acid is reported to be more effective as a decomposition reagent than either sulfuric or hydrochloric acid in the microdiffusion method for the determination of carbonate in dolomite, siderite, calcite, and magnesite.[32]

To prevent their interference in the electrolytic determination of lead as lead dioxide, the ions and solute species of chloride, bromide, arsenic, tin, and antimony can be removed as volatile species by evaporating to fumes with perchloric acid.[33] In this application the use of a nitric and perchloric acid mixture would be advisable to guard against explosion if appreciable organic matter is present.

Lichtin[34] determined chromium in chrome alums by iodometric titration after fuming with perchloric acid to oxidize chromium(III) to chromium(VI). Chitnis and coworkers[35] report that plutonium can be determined coulometrically after oxidation to plutonium(VI) by fuming with perchloric acid. The presence of iron(III) is necessary for *quantitative oxidation*.

According to Smith[36] the mineral alunite, $K_2Al_6(OH)_{12}(SO_4)_4$, dissolves readily in hot 72% perchloric acid if finely ground. Thus the determination of silica and the R_2O_3 metals can be carried out without recourse to sodium carbonate fusion.

WET OXIDATION OF ORGANIC MATTER

Determination of trace metals in organic matter, especially that of biological origin, has grown increasingly more common and widespread with the growing appreciation of the important influences exerted by trace metals in chemical and biological systems. Nondestructive methods of analysis, such as activation analysis and X-ray fluorescence, are preferred but not always practical for this purpose. Chemical methods require that the trace metals be released into solution prior to measurement. Sometimes simple treatment with a solvent suffices, but very often total destruction of the organic matter is necessary. Two general methods for this are dry and wet oxidations. Although each has its advantages, wet oxidation methods have proven more widely applicable and acceptable. Wet oxidations are versatile in that a variety of oxidants and solution combinations are available to provide a range of decomposition strengths and special advantages. Risk of loss by volatilization of sought-for elements or by their retention in vessels is much less due to the lower temperatures required. Moreover, mineral residues remain dissolved during wet oxidations, precluding the need for the sometimes difficult step of dissolving strongly ignited residues.

An excellent source of information on the destruction of organic matter has been compiled by Gorsuch.[37] Articles by Smith,[38-40] Middleton and Stuckey,[41] and Gorsuch[42] also provide critical reviews and useful general information.

Total decomposition of organic matter by wet oxidation is most efficient when perchloric acid is employed, either in combination with nitric acid or with nitric and sulfuric acids. Numerous studies support this conclusion. Mixtures consisting of only nitric and sulfuric acids are also satisfactory but less commonly used, because their action is slower without perchloric acid and special care must be taken to avoid charring. Once formed, char is extremely slow to be oxidized by nitric and sulfuric acids without perchloric acid. The use of nitric acid with perchloric acid provides an important safety margin against possible violent or explosive reactions. Easily oxidized matter is destroyed by the nitric acid before the perchloric acid becomes sufficiently concentrated to exert its strength on the remaining more difficulty oxidized matter.

After an extensive study on recovery of trace elements from organic materials, Gorsuch[42] concluded that the use of nitric and perchloric acids was not only very effective but trouble-free. The only significant loss was that of mercury. For the destruction of very obdurate materials, he found a mixture of sulfuric, nitric, and perchloric acids to be especially effective. Variable amounts of lead were lost, however, presumably due to coprecipitation of lead sulfate with calcium and other insoluble sulfates. Loss of lead was greatest from samples high in calcium. Gorsuch evaluated eight different oxidation methods; three involved wet oxidation, four were dry ashing procedures, and one was a hybrid. He concluded that wet oxidation with nitric and perchloric acids was the most satisfactory for recovery of all the trace metals investigated, with the single exception of mercury.

Trace element losses during mineralization of biological material by dry ashing and by wet oxidation with a mixture of nitric, sulfuric, and perchloric acids were investigated by Pijck, Hoste, and Gillis[43-45] using radiochemical methods. Elements investigated included Ag, As, Au, Co, Cr, Cu, Fe, Hg, Mn, Mo, Pb, Sb, V and Zn. Biological materials included blood, urine, powdered vegetable and muscular tissues. Dry ashing resulted in losses of the following elements, even at temperatures of 500-550°: Ag, As, Au, Fe, Hg, and Sb. Above 700° some loss of all of the elements studied occurred. Recoveries from wet oxidations were quantitative for all elements except As, Au, Fe, Hg, and Sb. Use of a reflux condenser in wet oxidations prevented loss of any of the trace metals.

Several other comparative studies have been conducted to determine which of various decomposition methods leads to the best recoveries of trace elements in organic matter. Allcroft and Green[46] found that wet oxidation with a mixture of sulfuric and perchloric acids gave the best recoveries of arsenic from animal tissues, in comparison with three other wet oxidation mixtures and a dry ashing procedure which involved addition of magnesium nitrate. According to Jackson,[47] recovery of iron from biological material is quantitative by wet oxidation with a mixture of nitric, sulfuric, and perchloric acids but incomplete by dry ashing, even though dry ashing be carried out with added sodium carbonate, calcium carbonate, or sulfuric acid treatment. Hiscox,[48] in comparing six different methods for destruction of plant materials in determination of cobalt, concluded that wet oxidation with nitric and perchloric acids gave the best recoveries.

Efficiency and Products of Wet Oxidations

Although a number of studies have been devoted to evaluating recoveries of trace elements from various compositions, relatively little attention has been paid to determining the completeness of destruction of organic substances by wet oxidation with perchloric acid and its mixtures with other acids. If clear and colorless solutions are obtained on wet oxidation, it is tacitly assumed that complete destruction of organic matter has been accomplished, particularly if quantitative recovery of trace elements is achieved. Such an assumption, however, can lead to serious error in some applications if organic matter still persists in solution. A knowledge of the identities and concentrations of residual organic matter, as well as inorganic products, is important in avoiding interference in subsequent measurements.

Martinie and Schilt[49] investigated the efficiencies of perchloric acid mixtures for the wet oxidation of various organic substances and attempted to identify any residual matter. Eighty-five different model compounds and common substances of a representative nature were subjected to prolonged wet oxidation with a mixture of nitric and perchloric acids. The final solution from each sample was then screened for organic residue by proton magnetic resonance spectrometry, ultraviolet spectrophotometry, and carbon microanalysis. Most solutions exhibited some ultraviolet absorption, and approximately one-half retained measurable carbonaceous matter. In general, compounds with N-methyl, S-methyl, C-methyl, and pyridyl moieties proved the most resistive towards wet oxidation. Glycine, alanine, proline, methionine, histidine, glutamic acid, and lysine were among the amino acids incompletely destroyed. Certain N-containing heterocycles, purines, and pyrimidines also resisted total destruction. Residual products were identified in a number of cases. Ammonium perchlorate, for example, was commonly found as a product of the wet oxidation of any N-containing compound. Most of those substances that proved resistive towards oxidation by the nitric and perchloric acid mixture yielded to total destruction in a reasonable period of time on treatment with a nitric, sulfuric, and perchloric acid combination. Complete oxidation of pyridine and 2,4,6-trimethylpyridine, however, proved especially slow. Vanadium(V), cerium(III), and copper(II) with selenized Hengar granules were found to exert catalytic influences on the wet oxidation of these and certain others.

The chemical compositions of solid residues obtained by heating to dryness various inorganic substances with a mixture of nitric and perchloric acids have been examined by Mansell, Tessner, and Hunemorder[50] using X-ray diffraction and infrared spectroscopy. Unfortunately, the complete identification of the residues proved difficult, even for relatively simple systems. Lack of crystallinity and complexity of mixtures, presumably of varying degrees of hydration and crystallinity, precluded reliable identifications by X-ray diffraction in many instances. Temperature control during heating to dryness was employed in relatively few cases, hence many of the results are difficult to interpret or reproduce. Since evaporation to dryness is not a common practice in wet oxidation procedures, the results obtained by Mansell and coworkers are of limited value. Their observation, for example, that iron and magnesium compounds are converted to the respective oxides could not apply to residues in solution. Further investigation of the fate of inorganic constituents and their identities after perchloric acid oxidations would be helpful in establishing the effectiveness and suitability of wet oxidation procedures for various analytical purposes. Few surprises are anticipated, however, based upon current knowledge of the chemical properties of perchloric acid and commonly encountered inorganic species.

The oxidation strength of perchloric acid can be regulated by control of temperature and concentration. Studies by Smith[40] indicate that hypophosphorous acid is not oxidized by boiling 30% perchloric acid, iron(II) is oxidized slowly to iron(III) by boiling 50% perchloric acid, and vanadium(IV) is readily oxidized to vanadium(V) with boiling hot 60% perchloric acid. Chromium(III) is easily oxidized to dichromate by boiling 72% perchloric acid. The redox potential is estimated to increase to approximately 2.0 volts on increasing the concentration of the boiling acid to 72% (boiling point 203°). Practical applications of graded oxidation potentials obtained by controlled concentrations have been described by Smith[40] and by Diehl and Smith.[51]

The major products of thermal decomposition of perchloric acid vapor at 279-471° in Pyrex vessels are chlorine, oxygen, and water, according to a study by Gilbert and Jacobs.[52] Small amounts of hydrogen chloride are also produced. Decomposition is first-order at all temperatures, with surface effects important at low temperatures. The ClO radical is possibly a chain carrier at low temperature. In another study[53] of the decomposition of perchloric acid, the products O_2, Cl_2, HCl, ClO_2, and Cl_2O, were found by chromatographic analysis. Chlorine produced during wet oxidations with perchloric acid can be readily removed after completion of the oxidation by dilution with water followed by boiling to drive out the chlorine.[14] Dilute perchloric acid does not generate more chlorine on boiling.

Oxidative degradation of glucose with 40% perchloric acid at 40° yields a mixture of products which includes gluconic, glucaric, glucuronic, tartaric, oxalic, citric, succinic, and levulinic acids.[54] The degradation is gradual and can be monitored by specific rotation, reducing power, ultraviolet spectrophotomery, and paper chromatography. Oxidative degradation of starch by perchloric acid, studied by the same methods, revealed the production of glucose and two ketoses and saccharic, glucuronic, gluconic and oxalic acids.[55,56] Total degradation of glucose and starch to carbon dioxide and water occurs if concentrated perchloric acid is employed at reflux temperature.[49]

Oxidation of hydrazine in perchloric acid in the presence of molybdenum(VI) as catalyst produces ammonium perchlorate, nitrogen, hydrogen, chloride, and water.[57] The reaction is zero-order in hydrazine and first-order in perchloric acid, with an activation energy of 19 kcal/mole.

Dichlorodinitromethane has been obtained as an oxidation product in the digestion of tobacco with mixed perchloric and nitric acids at 200°.[58] Collected by vacuum distillation, it exploded during distillation at atmospheric pressure. It was obtained also from the digestion of fir saw dust but not from nicotine, petroleum, charcoal, or graphite. The danger of explosion arises only when the dichlorodinitromethane is collected in concentrated form by distillation. No explosions have been reported by others with experience in wet oxidation of tobacco by nitric and perchloric acid mixtures.[39-49]

Procedures and Special Techniques

A great number of procedures, many differing only slightly, have been described for perchloric acid oxidations of organic and biological matter. Choice of which literature procedure to use is not generally critical because most will accomplish the intended purpose. There are, however, certain aspects that any given procedure should possess if it is to be both safe and effective. Easily oxidizable material should first be boiled with an excess of nitric acid present. Large samples (greater than a few grams) of organic matter should not be taken until small samples (0.1 g) of the same material have proven safe to oxidize. Any fat, oil, or volatile organic substance that is not miscible with perchloric acid should be decomposed with a mixture of sulfuric and nitric acid prior to boiling with perchloric acid, otherwise a violent reaction may occur in the hot vapor phase between the perchloric acid and organic vapors. Contrary to some published procedures, care should be taken not to evaporate to dryness solutions that contain heavy metal perchlorates or incompletely decomposed organic matter. The risk of explosion is too great. Wet oxidations should be carried out using fume eradicators[38] or special safety hoods that can be readily washed down periodically to remove build-up of acid condensates. Pyrex or Vycor reaction flasks should be employed. Also safety shields and safety glasses should be routinely used.

Most workers may prefer to follow the wet oxidation procedure decribed in the literature method specifically directed at their particular problem. For those undertaking possible revisions or new applications one of the methods described in the following paragraphs may prove helpful.

Plant material, certain animal products, foodstuff, and many different natural and synthetic products[49] can be wet oxidized effectively by the following procedure.

> Transfer an accurately weighed 1-g sample into a 125-ml conical flask and add 10 ml of 68% nitric acid and 5 ml of 70% perchloric acid. Place flask on a hot plate at low heat (under a fume eradicator[38] or in a hood, behind a safety screen) and heat slowly to boiling. Interrupt the heating when necessary to avoid excessive foaming. Increase the heating rate gradually so as to boil away the nitric acid in a period of approximately 15 min. During this period the temperature of the mixture will increase from about 120° to 140° and then rapidly to 203°, the boiling point of 72% perchloric acid. Interrupt the heating as needed to prevent foaming. Continue heating at the fuming point or gentle boil for 15 min. or until the solution is nearly colorless or only a faint yellow color persists. Allow the solution to cool, add 20 ml of distilled water, and heat to boiling to expel chlorine. After cooling and dilution to volume, aliquots can be taken for analysis of trace metals, phosphorus, and sulfur.

Animal tissues, proteins, heterocyclic compounds, purines, pyrimidines, certain polymers and other obdurate materials[49] can be wet oxidized effectively by the following procedure.

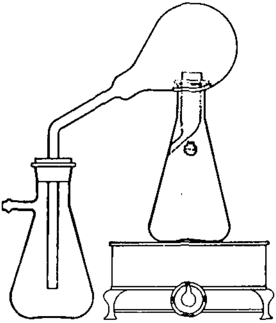

Fig. 4.1. Apparatus for performing wet oxidations in the open laboratory consisting of a Vycor or Pyrex flask fitted with a refluxing still head and fume eradicator. Gaseous products are removed by aspiration, and loss of spray is prevented by the reflux still head.

Transfer an accurately weighed 1-g sample into a 125-ml conical flask, add 5 ml of concentrated sulfuric acid, and heat at boiling for 15 min. After allowing the solution to cool, add 10 ml of 68% nitric acid and heat at a rate to cause the nitric acid to distill out over at least a 15-min. period. Cool the solution, add 5 ml of 70% perchloric acid, place the flask on a hot plate under a fume eradicator[38] or hood behind a safety screen, and heat at a rate to cause perchloric acid to reflux gently (about half-way up the sides of the flask) for 15 min. or until the solution is colorless or only faintly yellow. Allow to cool, diute carefully with 20 ml of distilled water, and heat to boiling to expel chlorine. If chlorine does not interfere in subsequent analysis, this final boiling step can be omitted. After dilution to a known volume, aliquots can be taken for analysis of trace metals.

A practical innovation has been devised by Monk[59] to minimize risk of violent reactions in perchloric acid oxidations. The sample of organic matter is first treated with fuming nitric acid and then added in small portions to boiling perchloric acid, maintained at its azeotropic concentration (72%), and oxidation is completed before addition of the next portion. Another approach by Monk,[60] suitable for controlled oxidation of cellulose, involves using a mixture of 7 ml of concentrated nitric acid and 3 ml of 72% perchloric acid for each gram of cellulose taken for analysis. The cellulose dissolves readily at 60-70°, and the resulting solution is then added in 5-ml portions to boiling 72% perchloric acid, completing the oxidation before adding the next portion.

An automated digestion system has been described by John[61] for use in nitric and perchloric acid oxidations of plant tissues. Samples are allowed to stand overnight in the acid mixture, then digested in a system enclosed by metal and heated with precise temperature control to slowly reach 203° and until wet oxidation is complete.

A rapid and safe method of heating mixtures of nitric and perchloric acids in a microwave oven has been dedescribed.[62] Evacuation and trapping of the acid, fumes, however, is troublesome.

Retention of elements (sulfur, arsenic, mercury, etc.) that form volatile products during wet oxidations can be achieved by use of special apparatus such as that designed by Bethge[63] or by Kahane and Kahane.[64] See Figure 4.2.

Smith and coworkers have investigated a number of special mixtures for wet oxidations. Sulfuric and perchloric acid mixtures enable control of oxidizing conditions at graded potentials by control of concentrations.[51] Periodic and perchloric acid mixtures serve effectively and safely at lower temperatures by promoting extensive degradation of high molecular weight species to smaller, more easily oxidizable fragments.[65] The generation *in situ* of perchloric acid through the action of nitric and hydrochloric acids on ammonium perchlorate provides slowly advancing oxidation potentials and minimizes risk of carbonization and uncontrolled reaction rates.[66]

Determination of Nonmetals

Nitrogen determinations by the Kjeldahl method are greatly facilitated by use of perchloric acid in conjunction with sulfuric acid to complete the digestion of samples in minutes rather than hours. Mears and Hussey,[67] the first to advocate use of perchloric acid as a digestion aid in Kjeldahl determinations, obtained accurate results under

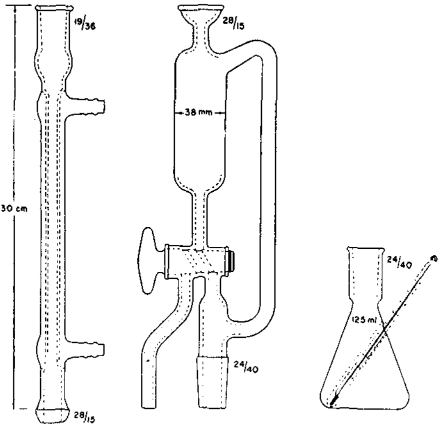

Figure 4.2. Bethge digestion apparatus for retention and/or collection of volatile products formed during wet oxidation of organic matter with perchloric acid mixtures. By suitable adjustment of 3-way stopcock condensed vapors can be returned to the digestion flask, collected in the air-cooled section of the apparatus, or delivered into an external vessel.

strict but easily controlled conditions. They noted loss of nitrogen when perchloric acid was used in excess of that necessary to decompose the organic matter. Best results were obtained using 1-g samples treated with 25 ml of concentrated sulfuric acid plus 1 g of copper sulfate and 2 ml of 60% perchloric acid, heated at such a rate that the digestion cleared in no less than 3 nor more than 7 min. and heated further at least 15 min. after clearing. Later investigators reported different degrees of success with the method when applied to a greater variety of substances.[68-71] Considerable controversy arose regarding the question of nitrogen loss; however, recent studies have helped to dispel much of the confusion. Moore and Diehl[72] demonstrated that low results for nitrogen can be caused by the action of chlorine or hypochlorous acid (produced from decomposition of perchloric acid) on ammonium salts. Diluting the mixture after digestion with a solution of sodium sulfite proved effective in destroying chlorine and hypochlorous acid, resulting in quantitative recovery of ammonia. Ginsburg and Shcheglova[73] found that no loss of nitrogen occurs in the digestion of plant material if the following procedure (similar to the Mears and Hussey procedure[67]) is employed.

> Place a 0.2-g sample of ground plant material into a 50-ml Kjeldahl flask and add 0.1 g of copper sulfate, 5 ml of concentrated sulfuric acid and 0.5 ml of 60% perchloric acid. Let stand for 30-60 min. Heat slowly for 5-7 min. until a chestnut-brown paste is formed and then more strongly until a light-blue clear solution forms in about 15-20 min. After cooling and dilution to a known volume, aliquots can be taken for determination of nitrogen, phosphorus, and potassium.

Batey and coworkers[74] observed that nitrogen loss can *be avoided by adding the perchloric acid in small amounts*, diluted with concentrated sulfuric acid. Others have stressed the importance of avoiding large excesses of perchloric acid.[75-77]

According to Sloane-Stanley and Jones[78] small scale digestions in test tubes with only perchloric acid are satisfactory for microdetermination of nitrogen in tissue sections and certain aldehyde derivatives.

Nitrogen, phosphorous, and potassium can be determined in a single sample following wet oxidation by a mixture of sulfuric and perchloric acid.[77,79,80]

Phosphorus and calcium in plant and animal materials have been determined rapidly and accurately in a single sample without interference, following wet oxidation with nitric and perchloric acids.[81] Phosphorus content of animal feeds have been determined rapidly with good results using sulfuric and perchloric acid digestion catalyzed by sodium molybdate.[82]

Sulfur has been determined in coal,[83] wood and paper pulp,[84] and rubber.[85-87] *The methods involve oxidation with* nitric and perchloric acids to destroy organic matter with conversion of sulfur to sulfate, which is subsequently precipitated and determined as the barium salt. A procedure based on the use of a mixture of periodic and perchloric acids for the determination of sulfur in coal has also been described.[88]

Wet oxidation methods have been successfully applied to the determination of arsenic in biological materials[89,90] and medicinals,[91] of silica in lungs[92] and plant matter,[93] and of iodine in organic compounds.[94]

Determination of Trace Metals

Applications of perchloric acid oxidations for trace metal determinations are so numerous that only selected examples are cited below. For a systematic review, covering most of the elements, the monograph by Gorsuch[37] should be consulted.

One of the earliest applications of perchloric acid oxidations for trace metal determinations was described by *Goss[95] in 1917 for the determination of tin in canned foods.* By the early 1930's, wet oxidations with perchloric acid mixtures had been employed by Fabre and Kahane[96] for the determination of As, Hg, Cu, Mn, and Cr in toxicological materials; by Gieseking, Snider and Getz[97] for the determination of Ca, Mg, K, and P in plant material; and by Gerritz[81] for the determination of Ca and P in biological materials.

Illustrative of the scope of perchloric acid oxidations, methods have been published for the determination of various metals in brain tissues,[98] coal,[88] feeds,[99] whetlerized carbon,[100] metal chelate compounds,[101] biological material,[102] plant material,[67,103] wines,[104,105] beer,[106,107] milk,[106] and milk products.[108]

Wet Oxidation is the method of choice for the destruction of organic matter in which lead, mercury, chromium and other volatile elements are to be determined. Webber,[109] for example, found that lead is lost from hay and pasture samples when dry ashed above 450° but not when oxidized with nitric and perchloric acids. Kozelka and Kluchesky[110] recommended use of sulfuric, nitric, and perchloric acids for the destruction of blood and soft tissue and the use of nitric and perchloric for bone in the determination of lead in biological samples. For the determination of mercury and other metals in fish and in coal, Feldman[111] avoided volatility losses in wet oxidation through careful control of refluxing and evaporation using temperature programing and an insulated air condenser. Excellent recoveries of chromium and of iron from different leathers, both chrome- and vegetable-tanned, were obtained by Smith and Sullivan[112,113] following wet oxidation with mixed nitric, perchloric and sulfuric acids.

In an investigation of different acid mixtures for wet oxidation of metal chelate compounds, Tsuchitani and coworkers[101] concluded that a 3 : 1 mixture of 62% nitric acid and 60% perchloric acid provided superior metal recovery in most cases. They recommended that metal content of a chelate be determined by decomposing 10-20 mg of sample with 10 drops of the acid mixture, heating until dense fumes of perchloric acid result, dilution with water and appropriate buffer, and titration with EDTA and appropriate metallochromic indicator.

TITRIMETRIC REAGENTS

Perchloric acid possesses a number of exceptional properties that greatly enhance its application in certain titrimetric determinations. It is one of the strongest acids known, its metal salts are water-soluble with few exceptions, its volatility is low, it is not oxidizable, it is not readily reducible in dilute solution, and its metal ion complexing ability is extremely weak.

The exceptional acidic strength of perchloric acid makes it the titrant of preference for the determination of weak bases, especially for nonaqueous titrimetry. Employed in conjunction with aprotic or predominately acidic solvents that do not exert an appreciable leveling effect on its strength, perchloric acid is superior to hydrochloric, nitric, and sulfuric acids for the titration of a host of organic and inorganic bases too weak to titrate successfully in aqueous solutions. Examples of solvents suited to its use in such applications include glacial acetic acid, dioxane, acetic anhydride, methyl isobutyl ketone, sulfolane, acetone, and acetonitrile. The number of weak bases successfully titrated in such solvents with perchloric acid is impressive and includes such very weak bases as the alkali halides, urea, and caffeine. For further details and literature references the interested reader is referred to an admirably concise book on the subject by Fritz.[114]

An interesting but apparently little used standard in acidimetry is 73.60% perchloric acid, prepared by vacuum distillation and described by Smith and Koch.[115] Distillation products obtained at 2 to 7 mm pressure varied only ±0.03% in acid content and ±0.0004 in specific gravity. Another perchloric acid-type acidimetric standard, pyridinum perchlorate, was proposed by Arndt and Nachtwey[116] in 1926.

For the accurate determination of carbonate in alkali and alkaline earth carbonates, Norwitz and Galan[117] recommend the use of perchloric acid in place of either sulfuric or hydrochloric acid. Treatment of samples with an excess of standard acid, followed by boiling to expel carbon dioxide, and titration of the excess acid with standard sodium hydroxide is uncomplicated by volatilization loss of acid or by precipitation of insoluble salts if perchloric acid is employed.

The inertness of dilute perchloric acid towards oxidants and most reductants affords an important advantage to its use as a solvent medium for various redox titrations, particularly those that require the presence of a strong acid to prevent metal ion hydrolysis or precipitation. Another significant advantage of perchloric acid in such applications is that its very weak complexing tendencies do not give rise to adverse alterations in formal potentials of the redox species involved in the titration. For such reasons, perchloric acid is commonly selected whenever an acid is required in adjusting solution conditions for redox titrimetry.

Formal potentials of the cerium(IV) — cerium(III) redox couple depend upon both the nature and the concentration of acid used in preparing the system. Highest formal potentials are attained using perchloric acid, providing thereby an extremely strong cerate oxidant suitable for the determination of a large variety of reducing substances. For example, Smith and Duke[118,119] employed cerium(IV) perchlorate to determine polyhydric alcohols, sugars, hydroxy-acids, and certain ketones. Similarly, Ignaczak and Dziegiec[120] determined p-quinone, p-aminophenol, p-phenylenediamine, p-*aminobenzoic acid, and sulfanilic acid.*

Metal perchlorates are occasionally selected as titrants for the precipitimetric or compleximetric determination of certain anions and organic complexing agents. Choice of the perchlorate rather than some other salt of the metal ion of interest can sometimes minimize interferences, solubility problems, competitive complexing, or coprecipitation error, depending on the nature of the titration reaction. An example of such an application is the use of mercury(I) perchlorate for the precipitation titration of halides and pseudohalides,[121-122] Mercurous perchlorate has also been recommended as a titrant for the reduction of iron(III) thiocyanate to the iron(II) state[123] and for the biamperometric determination of molybdate and gold.[124] Sharma and Gupta[125] employed thallic perchlorate for the oxidimetric determination of thiourea, thiosulfate, and sulfite.

PRECIPITATION AND EXTRACTION REAGENTS

The earliest analytical application of perchloric acid was for the precipitation and detection of potassium, as described by Serullas[126] in 1831. Through the use of 95% ethanol to further decrease the solubility of potassium perchlorate without adversely decreasing the solubilities of lithium, sodium, and the alkaline earth perchlorates, the method was developed into a quantitative procedure. Proving much simpler and more precise than the Fresenius method, which involves precipitation of potassium with chloroplatinate, the perchlorate method was widely employed[127-129] and extensively investigated[130-133] for possible further improvement. By the 1950's, however, the more rapid flame photometric method completely supplanted the perchlorate gravimetric procedure for the determination of potassium.

Use of perchloric acid to precipitate and recover potassium from sea salt brine or bittern has been studied by Bakr and Zatout.[134] Recovery proved more quantitative at low temperature, for high perchloric acid ratio, and with increasing potassium chloride concentration.

Sodium perchlorate has been recommended by Deniges[135] as a microchemical reagent for the precipitation of alkaloids, as well as for potassium, rubidium, and cesium. Ammonium perchlorate can be employed to precipitate cobalt, nickel, manganese, and cadmium salts from aqueous ammonia.[136] The detection and isolation of many different organic bases, alkaloids, carbonium, oxonium and thionium compounds can be achieved by precipitation with perchloric acid.[137-140]

The extraction of acid-soluble phosphorus compounds from plants is more reproducible with dilute perchloric acid solutions (0.2-0.5 M) than with either hydrochloric or trichloroacetic acid, according to Sokolov[141] When the extracts are neutralized for phosphate determination, interference from bivalent cations can avoided by addition of EDTA prior to neutralization.[142]

Perchloric acid has been found to be an efficient extraction reagent for the recovery of total endogeneous platelet serotonin as well as for the analysis of other platelet consituents such as nucleotides.[143]

Nucleic acids can be quantitatively extracted from animal tissues using 2% perchloric acid at 90° with 30-min. incubation, according to Webb and Lindstrom.[144] Conditions for the extraction of DNA and RNA from tobacco pollen with perchloric acid and sodium chloride have been investigated by Suss.[145] Use of perchloric acid extraction as an histochemical technique has been evaluated by several groups of investigators.[146-148] The following order of effectiveness in solubilizing membrane-bound proteins and non-electrolytes was observed by Hatefi and Hanstein:[148] $SCN^- > ClO_4^- >$ guanadine> urea> $Cl^- > F^-$.

The pronounced tendency for perchlorate ions to form stable ion pairs with large, symmetrical cations provides the basis for liquid-liquid extraction and subsequent determination of a great variety of substances. Examples include the spectrophotometric determination of cobalt with 8-quinolinol,[149] flame photometric determination of trace metals with 1,10-phenanthroline,[150] and the extraction-infrared spectrophotometric determination of cetyltrimethylammonium ions.[151]

DEPROTEINIZATION AGENT

Perchloric acid serves as an effective precipitant for protein removal prior to determination of other constituents in biological fluids such as blood, milk, and urine.[152,153] It is also useful for the isolation of protein-free metabolites, peptides, amines and amino acids.[153]

The behavior of serum albumin in acidic perchlorate solutions has been investigated by Cann.[154] Precipitation of albumin occurs first on lowering the pH to 3.7, but the precipitate redissolves progressively as the pH is lowered further and is redissolved completely at pH 3.2-2.3. Precipitation occurs again on lowering the pH below 2.3. Irreversible denaturation results on prolonged exposure to acidic perchlorate solutions. Tamura and coworkers[155] also have studied the precipitation of protein from cow serum, reporting that approximately 2-3% protein remained in the supernatant after treatment with 4 vols. of 3% perchloric acid.

Isolation of tissue mucoids (glucoproteins) and seromucoids from human and buffalo serums using perchloric acid followed by precipitation with ethanol has been reported by Kumar and coworkers.[156]

Comparison studies have demonstrated that perchloric acid is very satisfactory in place of trichloroacetic acid for use in deproteinization of biological materials prior to the determination of formaldehyde[157] and prior to citrate determinations.[158]

DRYING AGENTS

Anhydrous magnesium perchlorate affords a number of advantages as a drying agent in comparison with phosphorus pentoxide, its nearest competitor in dehydrating power.[159] Its capacity for water absorption is several times greater, it does not become sticky upon handling nor form channels through use, and it contracts in volume on absorbing moisture. Being neutral it is useful under conditions where the acidic action of phosphorus pentoxide interferes, and it can be recovered and reactivated repeatedly. Willard and Smith[159] found that anhydrous magnesium perchlorate and phosphorus pentoxide are equally efficient in drying moist air flowing at a rate not over 5 liters per hour. More precise investigations to determine the relative efficiencies of various chemical desiccants have since been performed. Bower,[160] employing phosphorus pentoxide as the ultimate standard of dryness, found a value of 0.002 mg of residual water per liter of air dried over anhydrous magnesium perchlorate. Diehl and Trusell,[161] using a cold trap cooled in liquid nitrogen to determine residual water directly by weight condensed, found that the residual content of moist nitrogen gas passed over anhydrous magnesium perchlorate was 0.2μg/l while that passed over phosphorus pentoxide was 3.6μg/1. A commercial form of magnesium perchlorate, Anhydrone, with hydrate water content corresponding to $Mg(ClO_4)_2 \cdot 1.48H_2O$ gave a value of 1.5μg/l. Thus, although some question may remain as to its relative efficiency compared to P_2O_5, the effectiveness of anhydrous magnesium perchlorate as a drying agent has been convincingly demonstrated. It combines high capacity with extraordinary affinity for moisture without loss of porosity or ease of handling.

Widely employed as a standard desiccant, anhydrous magnesium perchlorate is marketed under the trade names Dehydrite and Anhydrone as well as its generic name. Its use in laboratory desiccators was described by Smith, Bernhart and Wiederkehr.[162] Other applications have been reviewed by Smith[163] and by Druce.[164] It absorbs not only water but also ammonia, alcohols, and other highly polar vapors. Considerable risk of explosion arises if much alcohol or other easily oxidizable substance has been absorbed and the spent magnesium perchlorate is to be regenerated by heating. This should not be attempted; instead the magnesium perchlorate should be dissolved in water and recrystallized before dehydration. Methods for regeneration[165] and of determination of water content[166] of magnesium perchlorate desiccant have been described by Smith. A method for preparing the desiccant with added indicator to give visual evidence of its condition when spent has also been described.[167]

The trihydrate of magnesium perchlorate also serves as an effective desiccant.[168] Although less effective at ordinary and higher temperatures than the anhydrous salt, it can be prepared in a more porous form and thus is ideally suited for use in combustion train procedures for steel and organic analyses. At 0° it compares favorably with the anhydrous form in drying gases at equal flow rates.[159]

Barium perchlorate has been extensively studied as a dehydrating agent.[169-171] Although its efficiency is considerably less than that of anhydrous magnesium perchlorate, it is easier to prepare and regenerate in anhydrous form. Heating between 140 and 400° drives out absorbed water without fusion or physical disruption of the solid. In drying effifiency it is comparable to anhydrous calcium chloride.

Bower[160] found 0.82 and 0.36 mg residual water per liter of *air dried over anhydrous barium perchlorate and calcium* chloride, respectively. Diehl and Trusell[161] observed 0.60 and 0.99 mg residual water per liter of nitrogen dried over barium perchlorate and calcium chloride, respectively. Barium perchlorate also is an efficient absorbent for ammonia and other small polar molecules.

Although considerably limited in scope of application, *an azeotropic solution* of perchloric acid (72.5% $HClO_4$, b.p. 203° at 760mm) exerts a strong dehydrating action at its boiling point. Willard and Cake[3] greatly improved and simplified gravimetric silica determinations by taking advantage of this property. Silica in metals, silicates, limestones, etc. is rendered more insoluble, more quantitatively recoverable without necessity of evaporation to dryness and baking, and less contaminated when concentrated perchloric acid is employed in place of hydrochloric acid. Presumably other hydrous oxides could be similarly dehydrated if inert to boiling 72% perchloric acid. To be practical the dehydration should be essentially irreversible so that perchloric acid can be washed from the dried solid.

MISCELLANEOUS

An important innovation in the widely used Babcock method[172] for the determination of butterfat in milk and milk products was introduced by Smith, Fritz, and Pyenson[173] in 1948. By replacing concentrated sulfuric acid with a mixture of equal parts by volume of 72% perchloric acid and glacial acetic acid, they demonstrated that only one centrifugation was necessary. No charring of sugar occurs, and the presence of various flavor additives and egg products do not interfere. Their method is especially advantageous in application to ice cream.

In a study of methods for determining fat in meat and fish products, Rudischer[174] reported that the fat content is released from 5-g samples by digestion with either 5 ml of a 1:1 mixture of 70% $HClO_4$ and 100% H_3PO_4, 5 ml of a 1:4 mixture of 70% $HClO_4$ and 85% H_3PO_4, or 20 ml of 30% potassium hydroxide.

Perchloric acid has found use as a chromogenic reagent for the detection and determination of steroids. Extraction into chloroform followed by treatment with perchloric acid and heating at 56° yields different colors for various steroids.[175] Color reactions of steroids and some thirty different aromatic aldehydes with perchloric acid have been described by Few.[176] Kimura and Harita[177] studied the reaction of testosterone with perchloric acid, concluding that the chromophore is produced from isomeric olefins which are intermediates in the chromogenic reaction.

Detection of sugars and sugar derivatives on paper chromatograms[178] and cellulose thin layers[179] can be achieved by spraying with perchloric acid solutions. Godin[180] employed an aqueous solution of perchloric acid and vanillin for the detection of sugar alcohols and ketoses. Others[181-183] found that this same spray mixture also detected deoxysugars sensitively. Nagaswa and coworkers[179] observed that the use of aqueous perchloric acid alone greatly reduced the sensitivity of detection of sugar alcohols thereby increasing the selectivity of the test for deoxysugars and ketoses. They performed a comprehensive and systematic study of color reactions of sugars, sugar derivatives and related compounds after chromatographic separation on cellulose thin-layers syrayed with aqueous perchloric acid (5%), dried at room temperature, and heated for 10 min. at 80°. Their paper[179] should be consulted for details and applications. The use of perchloric acid as a spray reagent for the detection of amino acids in paper chromatography has been described by Giri.[184] More recently, a simple and specific determination of ketohexoses with urea and perchloric acid has been reported.[185]

Use of a hydrogen-perchloryl fluoride flame for flame spectrophotometry has been investigated by Schmauch and Serfass.[186] The flame is easily controlled, has a very low background, produces primarily atomic lines and metal fluoride and chloride band radiation, and the spectra produced for many metals are suitable for analytical purposes. Oxide bands of refractory metal oxides were only a minor interference, despite high oxygen content in the flame.

Addition of ammonium perchlorate to the sample solution in atomic absorption spectrophotometry is recommended by Oguro for the elimination of iron interference in determination of chromium[187] and for enhancement in the atomic absorption of europium.[188]

Use of mixed hydrochloric and perchloric acids in forced-flow anion exchange chromatography, investigated by Seymore and Fritz,[189] permits several separations that are otherwise impractical due to the inability of hydrochloric alone to elute certain metal ions. Examples include the separation of arsenic(III), antimony(III), and bismuth(III) and the separation of nickel(II), palladium(II), and platinum(IV).

Other applications of perchlorates in analysis include the following: silver perchlorate solution as an absorbent for acetylene in the determination of lithium carbide in metallic lithium,[190] lithium perchlorate trihydrate as a source of water for coulometric generation of hydrogen ions in nonaqueous titrimetry of weak bases,[191] perchlorate ion as a probe in NMR studies of protein anion binding,[192] perchloric acid as an oxidant for dithionite-citrate in the determination of reductant soluble iron phosphate in soil,[193] and magnesium perchlorate as an oxidant in the determination of biochemical oxygen demand of waste waters.[194]

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CHAPTER V

APPLICATIONS IN ORGANIC SYNTHESIS, INDUSTRY, AND COMMERCE

Catalysts

Esterification and Acetylation. Perchloric acid serves as a highly effective catalyst in the acetylation of cellulose and has been extensively studied in this regard due to the considerable commercial importance of cellulose esters.[1,2] The catalytic activities of various acids in acetylation of cellulose have been found to parallel their Hammett acidity functions in the acetylating medium,[3] with perchloric acid exhibiting the greatest activity. Studies suggest that the catalytic activity is associated with acetyl perchlorate, formed through reaction of perchloric acid with acetic anhydride. The rate of formation of acetyl perchlorate is considerably faster than the rate of cellulose acetylation,[4] and the equilibrium constant for the formation reaction is 33 l/mole.[5] Kinetics of the reaction between perchloric acid and acetic anhydride also have been studied.[6,7] Patent claims by Lamborn[8] indicate that the catalytic action of perchloric acid can be easily controlled by addition of metal chlorides, bromides, phosphates, or sulfonates. Some degradation occurs during acetylation of cellulose catalyzed by sulfuric and perchloric acid mixtures.[9] If sulfuric acid is added after completion of acetylation with perchloric acid, formation of sulfo-esters is prevented.[10]

Processes have been patented for the preparation of acetic acid esters of hydroxyethyl cellulose using perchloric acid and zinc chloride as catalyst[11] and for the preparation of mixed esters of cellulose using 0.2 to 0.5 per cent perchloric acid.[12] A process for treating wood by impregnation with a solution of magnesium perchlorate in acetic anhydride followed by heating has been reported to increase the weight of wood by formation of cellulose acetate.[13]

Esterification of acetic, stearic, or benzoic acid in ethanol is catalyzed by alkaline earth chlorides, bromides, nitrates, and perchlorates.[14] Stearic and acetic acids behave similarly, both with and without catalysts; their rates of esterification at 80° increase 500-fold with 0.5 *N* calcium perchlorate. Calcium bromide provides less catalytic activity, calcium chloride even less, and calcium nitrate the least. Benzoic acid completely resists esterification in ethanol at 80° but reacts readily in the presence of calcium perchlorate.

Ring acetylations with acetic anhydride are catalyzed as effectively by sodium perchlorate and acetyl perchlorate in glacial acetic as by acetylium perchlorate or perchloric acid, according to Mathur and coworkers.[15] A 30 to 50 per cent conversion of monohydric or polyhydric phenol ethers into corresponding acetophenones can be generally achieved within 4 to 6 hours at 40 to 60°. Perchloric acid is a much more effective catalyst than zinc chloride for acetylation of quinones with acetic anhydride.[16] Acetylation of hydroxydeoxybenzoins with acetic anhydride and perchloric acid has been reported.[17] The catalytic acetylation of aromatic and heterocyclic compounds in the presence of perchloric acid has been described by Dorofeenko.[18]

Polymerization. Perchloric acid, acetyl perchlorate, and various metal perchlorates find application as catalysts in a variety of polymerization reactions. The polymerization of styrene and its catalysis by perchloric acid has been studied most extensively because of its considerable commercial importance.

Styrene undergoes polymerization in the presence of phenol, using acetic acid as solvent and perchloric acid as a catalyst, at a rate proportional to the square of the perchloric acid concentration, according to Lilley.[19] Pepper and Reilly[20] found first order kinetics for the polymerization in ethyl chloride, dichloroethane, and carbon tetrachloride-dichloroethane, catalyzed by perchloric acid. From a study of the mechanism of polymerization of styrene in carbon tetrachloride initiated by anhydrous perchloric acid, Hamann and coworkers[21] proposed that the rate determining step may be formation of an ion-pair between perchlorate and a carbonium ion in association with neutral molecules of styrene. The kinetics of polymerization in methylene chloride, measured by stopped-flow methods at 0 to —80°, indicate the presence of a transient intermediate.[22]

Use of acetyl perchlorate as a catalyst for the selective dimerization of styrene to 1,3-diphenyl-1-butene[23] and for the dimerization of methylstyrenes[24] has been described by oxymercuration of D-glucal triacetate with mercuric perchlorate has been described by Honda, Dulenko, and Zhdanov.[55]

Solvents

In addition to its use as a solvent for various inorganic reactions and substances, perchloric acid has proven useful as a solvent for certain organic materials, notably cellulose and cellulose derivatives,[56,57] acrylonitrile polymers,[58,59] and crystalline methacrylonitrile polymers.[60]

Perchloric acid can be used alone or in conjunction with other solvent media to selectively dissolve alcohols, ketones, and amines from resinous materials.[61]

The dissolution of fir cellulose by 45-65% perchloric acid has been found to be preceded by formation of addition compounds of the oxonium type.[62] Optimal conditions for formation of addition compounds at 20° are 62 to 65 per cent perchloric acid and 15-min. treatment time. Extensive dissolution of the cellulose occurs with longer treatment. No ester formation was observed.

Explosives, Propellants, and Pyrotechnics

The use of ammonium perchlorate as an ingredient in various explosive mixtures was first described by Oscar Carlson in British and Swedish patents granted in 1897. Since that time various perchlorates have been extensively studied and implemented in a great variety of explosive and combustive devices. Much of the information available on the subject is in the patent literature. Undoubtedly a great deal more is known but restricted to the realm of classified and trade secret information. A brief survey of the uses of perchlorates is provided in the following paragraphs. For further details and literature citations the reader is referred to reviews by Gale and Weber,[63] Kast,[64] Médard,[65] and Girard.[66]

Inorganic perchlorate explosives generally consist of mixtures of either ammonium or potassium perchlorate as oxidant with sulfur and/or various organic materials as fuels. Special additives are commonly present also to modify shock sensitivity, caking qualities, products of combustion, explosive characteristics, bulk density, and water-repellancy. Explosive mixtures that contain potassium perchlorate are generally less powerful than those with ammonium perchlorate and are suitable for special purposes, such as blasting soft rock and coal deposits. Numerous composite explosives have been investigated, including ammonium perchlorate in combination with other oxidants such as nitrates, nitrocompounds, and organic perchlorates. With a large variety of choices available among oxidants, fuels, and additives, the number of different combinations and compositions that can be formulated is enormous. An almost endless array of composite explosives can be formulated, each with its special advantages and limitations.

Perchlorate explosives afford certain advantages over dynamite and other nitroglycerine explosives. They are safer to handle, less sensitive to shock, considerably less affected by freezing, free from exudation in warm climates, and relatively nontoxic. Their explosive action is somewhat slower and extends laterally more than dynamite, but they are capable of producing relatively greater destructive effects. Perchlorate explosives can be formulated in a great variety of compositions, permitting their adaptation to a wide range of purposes. For example, a suitable choice between explosive compositions enables fragmentation of hard rock into either minute pieces or large blocks.

Organic perchlorates are unique as explosives in as much as the oxidant and combustible material are both present in the same molecule. Consequently, they tend to undergo very rapid reaction and violent explosion when detonated. The perchlorates of guanidine, dicyanodiamidine. aniline, pyridine, methylamine, hydrazine, and metal hydrazines are typical examples.

Ammonium perchlorate is manufactured on a large scale for use in preparing propellant mixtures formulated to undergo relatively slow burning so as to produce nearly uniform acceleration in propulsion of rockets, missiles, air planes, and other projectiles. Both liquid and solid propellant mixtures are prepared. An example of the liquid kind consists of a suspension of ammonium perchlorate in nitromethane. Solid propellants are basically of two types: composite and homogeneous. The former consist of solid oxidant particles dispersed in a matrix of the fuel; the latter are colloidal mixtures of the oxidizer and fuel in which the separate phases are not readily distinguishable. Commonly used solid fuels include natural and synthetic polymers, such as polysulfide rubber, hydrocarbon rubbers, epoxy resins, and polyester resins. Composite propellants that contain potassium perchlorate as the primary oxidant generally have higher burning rates, higher flame temperatures, and denser smoke production compared to those with ammonium perchlorate as principal oxidant. Homogeneous or colloidal propellants generally contain a nitrate or nitro compound as the major oxidant and a perchlorate as a supplemental oxidant. Numerous recent patents describe various organic perchlorates as oxidants for use in rocket propellant compositions.[67-75]

Relatively slow burning compositions are required for time fuses, signal flares, and pyrotechnics. Many of the formulations described to date contain one or more metal or organic perchlorates to serve as auxiliary oxidants. Some recently described examples include the use of zirconium perchlorate in pyrotechnical lacquer for primers,[76] ammonium and potassium perchlorates in signal flares,[77] tungsten perchlorate in time delay pyrotechnic compositions,[78] and potassium and titanium perchlorates in firecrackers.[79]

Mixtures of sulfamic acid and ammonium perchlorate have been described in a patent[80] for use in producing a dense smoke or fog. Ignition of an optimum mixture of the two components results in a rapid, self-sustaining reaction yielding hydrogen chloride and sulfur trioxide as combustion products. In the presence of moist air these products absorb water and give rise to a dense cloud or fog-like mist.

Electrolytes

Electropolishing. The technique of electrolytic oxidation is extensively employed to bright polish metal surfaces and to remove surface irregularities in high precision machining of metal parts. In this electrolytic process the metallic sample is immersed in a suitable electrolytic solution and a controlled electric current is passed between the sample as the anode and some suitable metal serving as the cathode. Two important requirements of the electrolyte are that (1) it is not readily oxidized, and thus does not compete with the oxidation of the anodic sample, and (2) it forms readily soluble salts with the metal ions produced by anodic reaction of the sample to be bright polished. Perchloric acid or its salts possess both of these desirable attributes and thus find frequent application as electrolytes in electro-plating baths. Nonaqueous solutions are most commonly employed, because their use facilitates control of current densities, over-voltage effects, and solubilities.

Among the first to report studies on electropolishing, Jacquet and Rocquet[81] found that iron and steels can be electrolytically polished in a bath consisting of acetic anhydride and perchloric acid, kept below 30°. A d.c. voltage of 50 v., a current density of 4 to 6 amps/dm^2, and an aluminum cathode were employed. Their procedure was evaluated further by Pellissier, Markus, and Mehl[82] and applied to the electropolishing of tin, aluminum, lead, and alloys of lead and tin. Adjustment of the current density is important in electropolishing in order to prevent evolution of gas at the anode at too high densities or objectionable etching of the sample surface at too low a current density.

Numerous electrolytic solutions have been investigated and applied in electropolishing of metals. Those which contain either perchloric acid or a metal perchlorate in their formulation include the following: (1) acetic anhydride and perchloric acid,[81-84] (2) acetic acid and perchloric acid,[85-87] (3) acetic acid and sodium perchlorate,[88] (4) ethanol and perchloric acid,[89-91] (5) methanol and perchloric acid,[92,93] (6) ethanol, ethylene glycol monobutyl ether, and perchloric acid,[94,95] and (6) dimethylsulfoxide and perchloric acid.[96]

Procedures for bright polishing the following samples have been published or described in patents: aluminum and its alloys,[82-84,88-92] iron and steel,[81,85-88,90,93] nickel and its alloys,[87,95] razor blades,[97] tin and lead alloys,[82] and zirconium and its alloys.[94]

The hazards associated with the use of perchloric acid in electropolishing baths have been emphasized and reviewed by various writers.[98-100]

Voltaic Cells and Batteries. Use of perchlorate salts in electrochemical cells and batteries have received considerable attention in recent years owing to the improved performance, lower concentration polarization, and longer shelflife afforded by such electrolytes. Considering the commercial importance of electrochemical devices it is not surprising that much of the information is of a proprietary nature. A brief summary of the literature and patents on the subject is provided in the following paragraphs. The cells are classified according to anode material employed.

Aluminum anode cells, with aluminum perchlorate electrolyte and manganese dioxide cathodes have been described by Schumm.[101] These dry cells are similar to Leclanche dry cells, but they possess relatively low concentration polarization and low activation polarization which compensate for their relatively high internal resistance. Corrosion resistance of aluminum is satisfactory in the presence of the electrolyte buffered at pH 0 to 4; however, gas production and swelling during discharge cause problems in sealing the cells against leakage.

Lead storage cells, employing perchloric acid in place of aluminum is satisfactory in the presence of the electrolyte Cădariu and Schonberger.[103] Although better performance is claimed, some difficulty arises in fabricating lead dioxide adherent electrodes.

Lithium batteries, attractive for their low weight, have been explored extensively. Gaines and Jasinki[104] described lithium - nickel sulfide batteries and their design to improve performance at high discharge rates and at low temperatures. A solution of lithium perchlorate in tetrahydrofuran is employed as the electrolyte in a patented lithium - metallic chromate battery.[105] According to the patent claims, it is light-weight, high in energy density, and both chemically and dimensionally stable. Another battery of high energy density, also patented, is the lithium - copper sulfide battery described by Garth.[106] Its electrolyte consists of a solution of lithium perchlorate in 1,3-dioxolane. A self-sealing battery with a nonaqueous electrolyte was patented by Alder,[107] consisting of a lithium anode, a copper sulfide cathode, and an electrolyte containing by weight 10% lithium perchlorate, 23% 1,2-dimethoxyethane, and 67% tetrahydrofuran. A German patent[108] describes electrolyte solutions of high electric conductance for use in lithium batteries consisting of 1 - 2.5 *M* lithium perchlorate in mixtures of dioxolane or propylene oxide with 10 to 50% propylene carbonate or ethylene carbonate. A lithium-copper sulfide battery, in which the anode chamber containing lithium perchlorate in dimethylformamide is separated by means of a membrane from the cathode compartment containing sodium polysulfide, has been described in a recent German patent.[109]

Magnesium batteries are relatively light in weight and possess high energy densities, especially those that incorporate perchlorate salts as electrolytes. It is reported that a magnesium - silver(II) oxide cell with an electrolyte solution 2.4 *M* in sodium perchlorate, 1.6 *M* in lithium perchlorate and 0.1 *M in sodium borate can be operated over several weeks at an average discharge voltage of 1.6 volts.*[110] *A German patent* has been granted to Bauer and Winkler[111] for a magnesium - manganese dioxide battery employing a depolarizer containing 7.4 to 24% magnesium perchlorate, 6% carbon black, 2% barium chromate, 0.5% magnesium oxide, and 57% manganese dioxide. Garbacher[112] received a British patent for a high energy density electrochemical cell comprised of a magnesium anode, a cathode of perforated stainless steel coated with sintered nickelous ammonium sulfate and an organic-bound mercuric oxide paste containing carbon black, and an electrolyte of 5 *N* magnesium perchlorate containing 5% *lithium perchlorate incorporated into fibrous carriers.*

Various investigators have reported achieving improved performances for zinc - manganese dioxide dry cells (Leclanche cells) by using zinc perchlorate as the electrolyte in place of zinc chloride. For example, significant improvement in retention of capacity at high temperature is claimed.[113] Machat and Sohm[114] found that a Leclanche-type cell with an electrolyte containing 1.5 M zinc perchlorate and saturated with zinc hydroxide provided 4-times the capacity of a conventional Leclanche cell after aging 2 months at 60°. These same authors[115] also found that (1) corrosion of the zinc anode in a Leclanche-type cell is greatly reduced by replacing zinc chloride with zinc perchlorate and (2) the capacity on both continuous and intermittant discharge is improved without loss of other favorable properties. According to Watanabe and coworkers,[116] Leclanche-type dry cells with zinc perchlorate and ammonium chloride as electrolyte give good discharge characteristics under heavy loads.

A zinc - lead dioxide storage cell has been described[117] that contains 40% perchloric acid and resists freezing even at —56°.

Machat and Sohm[118] obtained a patent for a zinc - mercuric oxide battery containing zinc perchlorate electrolyte which is suitable for use in electrical measuring instruments and watches because of its freedom from gas formation.

Perchlorate salts are effective in alkaline electrolytes for preventing passivation of primary and rechargeable cells.[119] For example, calcium perchlorate and sodium hydroxide are employed in an alkaline battery patented by Berger and Dietlin.[120] Tetrabutylammonium perchlorate is employed in nonaqueous electrolyte solutions patented by Katv and Saito.[121]

Miscellaneous. Concentrated perchloric acid is employed in a carbon fuel cell patented by Becker.[122] The cell consists of a carbon cathode in contact with sulfuric acid, a porous clay diaphragm, and a copper or carbon anode in perchloric acid. It operates by oxidation of carbon at 20 to 90°.

A carbon fuel cell utilizing lithium perchlorate and nitrogen dioxide dissolved in a mixture of propylene carbonate and acetonitrile as a nonaqueous electrolyte has been patented by Schlaikjer.[123]

Lead perchlorate has been recommended as a highly soluble salt for use in electroplating and refining of lead.[124,125]

Ozone can be electrogenerated from 40% perchloric acid using platinum anodes refrigerated at —60 to —65°. Yields and current efficiencies improve with increasing current densities and decreasing temperatures.[126]

Animal Feed Additives

Considerable attention has been devoted by Russian investigators to the use of ammonium, sodium, and potassium perchlorates as stimulants for increasing the weight of farm animals and poultry. According to Solun and coworkers, who first reported on the subject,[127,128] the perchlorates exert a significant thyrostatic effect when added to feed rations of cattle and broilers that leads to increased weight gains of up to 20%. The perchlorates are metabolized and completely eliminated, mainly *via* urine, within 24 to 48 hours.

Young bulls fed at a daily rate of 2.5 mg of ammonium perchlorate were found to have gained 19 kg or 17.8% more than controls after 90 days.[129] Their thyroid weights did not change significantly in this time, but some marked differences in microstructure were observed. Similar studies revealed that weight gains depend on feed type.[130-132]

Ammonium perchlorate administered to oxen in their feed increased the deposition of internal fat by 39% and caused a slight but noticeable effect on the aroma of the meat.[133] Ammonium perchlorate administered daily to bulls in their feed over a 7-month period (2.5 mg NH_4ClO_4/kg body weight) resulted in increases in body weights of 17.3 to 20.7%, meat yields of 9.4%, and fat yields of 22.4%.[134] Ammonium perchlorate in the diets of young rams and ewes led to increased weight gains without affecting meat quality.[135]

The effect of ammonium perchlorate on nitrogen metabolism in young chickens has been investigated by Kurilova.[136]

Explosion hazards associated with storage and handling of weight stimulators containing perchlorate salts can be decreased by addition of other salts, according to Yakimenko and coworkers.[137]

Miscellaneous

Anhydrous magnesium perchlorate and barium perchlorate serve as highly efficient drying agents for gases. They are also useful for removing small amounts of polar compounds from inert gases. Further details are described in Chapter IV.

Potassium perchlorate is employed together with strontium azide and boron in a gas-forming composition which is suitable for the rapid inflation of automobile safety bags. Ignition of the gas-forming composition can be rapidly achieved in the event of an automobile collision by use of ignition mixtures of boron, zirconium, aluminum, and/or magnesium with lithium perchlorate, sodium perchlorate, potassium perchlorate, ammonium perchlorate, and/or potassium nitrate.[138]

A patented composition to ignite charcoal briquets contains 15 to 16% potassium perchlorate, 4 to 6% metal nitrates, and 78 to 81% carbonized matter.[139]

Use of iron and potassium perchlorate mixtures in the form of pellets to serve as heat generating material or "thermal reservoir pellets" for initiating action of thermal batteries has been described by Bush.[140,141]

Lead borate glass solder, used for connecting the front and funnel parts of color television tubes, can be selectively dissolved in 0.4 to 1.6 *M* perchloric acid at or below 85°.[142] It can also be dissolved in 0.5 to 6 *M* perchloric acid at 21° in the presence of ultrasound.[143]

Perchloric acid has been employed as a drilling agent and disinfectant in the treatment of dental canals,[144] as a component in etching solutions for production of semiconductor devices,[145] and in solutions to passify or prevent corrosion of iron[146] and steel surfaces.[147]

Addition of small amounts of sodium perchlorate to cooling-lubricants employed in machining of metals is reported to reduce friction and increase the wear life of high-speed cutters.[148]

An antipollution system for internal combustion engines has been patented based upon use of oxygen generated by heating lithium perchlorate in the presence of manganese dioxide catalyst.[149] By elimination of air, oxides of nitrogen are eliminated.

Use of aluminum perchlorate in styptic preparations[150] and of diazonium perchlorate in diazo copying compositions[151] have been described in recent patents.

Quaternary ammonium perchlorates have been found useful as sensitizing agents for photographic emulsions.[152,153]

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CHAPTER VI

CHEMICAL ANALYSIS OF PERCHLORATES

Detection Methods

Methods for the detection of perchlorate ions generally involve precipitation, extraction, or decomposition of perchlorate to give characteristic, identifiable products. Invariably, the methods lack specificity unless either prior separations are performed or reliable confirmatory tests are conducted.

Milligram amounts of perchlorate (5 to 50 mg) can be detected and identified with considerable confidence by precipitation with tetraphenylarsonium chloride, followed by infrared examination of the precipitate in a potassium bromide disc.[1] Although perrhenate, permanganate, periodate, pertechnate, molybdate, chromate, and tungstate also form insoluble tetraphenylarsonium salts, none exhibit an intense absorption band at 9.12 μm (1096 cm^{-1}) as does the perchlorate. For greater sensitivity, particularly when the perchlorate concentration is too low to provide sufficient precipitate, perrhenate can be added to the sample so that tetraphenylarsonium perchlorate will coprecipitate and thus be collected by the precipitate of tetraphenylarsonium perrhenate.[2] This method is reportedly[3] capable of a sensitivity of 0.03 μg of perchlorate per ml, with a coefficient of variation of approximately 10%.

Diphenyliodonium chloride can be used in place of tetraphenylarsonium chloride to precipitate perchlorate and other polyatomic anions for identification by infrared spectrophotometry.[4] In a KBr disc, the perchlorate salt is identified by strong absorption bands in the 1080 to 1140 and 620 to 634 cm^{-1} regions.

For the detection of microgram amounts of perchlorate the method of Feigl and Goldstein[5] is suitable, provided that nitrates and halates are absent or first removed by fuming with concentrated hydrochloric acid. The test sample is fused with cadmium chloride while testing the gas phase above the melt for the appearance of chlorine, which will cause a test paper impregnated with thio-Michler's ketone to turn blue or a paper with a fluorescein-bromide mixture to turn red. Detection of chlorine by either test paper indicates the presence of at least 1 or 5μg, respectively, of perchlorate in the test sample. A similar method, involving fusion with zinc chloride, was described by Gooch and Kreider[6] in which 50 μg of perchlorate was detected.

To distinguish between perchlorate and some 26 other anions the systematic qualitative analysis scheme of Belcher and Weisz[7] as extended by Hayes[8] can be followed. The final supernatant, remaining after the sequence of separations described by Belcher and Weisz, is treated with a slight excess of 4 N sulfuric acid to remove barium ions. Addition of 4 drops of saturated zinc sulfate and 1 drop of 0.03 per cent methylene blue to 1 drop of the barium ion-free supernatant test solution will result in a color change to purple-red if perchlorate is present.

Simple precipitation tests with various cations, although subject to many interferences, are useful for indicating the absence or possible presence of perchlorates. These include tests with methylene blue (free of zinc salts) to give a violet precipitate,[9,10] potassium chloride to precipitate perchlorate from ethanol-water solution,[11] rubidium chloride and potassium permanganate to yield a colored precipitate of rubidium perchlorate,[12] strychnine sulfate,[10] tetraphenylarsonium chloride,[13] and copper(II) sulfate-pyridine solution.[14]

Perchlorates may also be detected by fusion with sodium carbonate to yield chlorides which yield silver chloride on treatment with silver nitrate.[10] Chlorates and chlorides interfere.

A colorimetric detection procedure[15] is suitable for the detection of 3 μg or more of perchlorate but suffers from interferences by trace amounts of iodide, thiocyanate, periodate, perrhenate, and cetain metal ions as well. The test is based upon the extraction of perchlorate into methyl isobutyl ketone in the form of an ion-association complex with azide and a copper(II) complex of 2,2′-bipyridine. Extractability of the yellow copper(II) complex is dependent on the presence of both azide and perchlorate anions. The limit of detection can be lowered to 0.15 μg of perchlorate by applying the Weisz ring-oven technique to the extract.[15]

Separation Methods

Because so many possibilities exist for interference, the most reliable methods for the identification or determination of perchlorates in complex mixtures are those that incorporate some separation step to either remove suspected interferences or isolate the perchlorate before measurement. Chromatographic separations have proven to be highly effective in this regard. Solvent extraction is often useful but not always entirely effective. Separation by systematic precipitation procedures, although feasible,[7,8] are rarely employed.

Partition chromatography has proven to be one of the most effective chromatographic methods for resolving mixtures of chloride, chlorite, chlorate, and perchlorate. For example, Harrison and Rosenblatt[16] employed paper partition chromatography to successfuly resolve mixtures of these anions on Whatman No. 1 filter paper. Starting with as little as 10 *μg of each ion, they obtained well-defined chromato*grams in about four hours using a mobile phase consisting of a mixture of isopropyl alcohol, water, pyridine, and concentrated ammonium hydroxide (15:2:2:2). The following R_f values were observed for the anions: Cl^-, 0.25; ClO_2^-, 0.34; ClO_3^-, 0.50; and ClO_4^-, 0.65. The perchlorate band was located by spraying with 0.2 per cent aqueous methylene blue solution.

Thin-layer partition chromatography was used by Peschke[17] to separate halites, halates, and perhalates on silica gel and modified silica-alumina layers. A mixture of n-butanol, acetone, concentrated ammonium hydroxide, and water (40:50:10:5) served as eluent. Chromatograms with a specific color for each ion were developed by spraying with a solution of 0.93 g of aniline and 1.66 g of o-phthalic acid in 100 ml of water-saturated n-butanol followed by heating at 130° for 20 *min. Thielemann*[18] *employed a similar chromatographic* procedure to separate and identify the oxy-anions of chlorine produced from chlorine dioxide treatment of drinking water. Using specially activated silica gel plates (impregnated with 2:1 acetone-formamide and dried at 120°), an elution mixture of 60:25:5:10 n-butanol-acetone-ammonium hydroxide-pyridine, and spraying with bromocresol purple to detect the spots under ultraviolet light, he obtained the following R_f values: ClO_2^-, 0.36; ClO^-, 0.38; ClO_3^-, 0.68, and ClO_4^-, 0.64. Chloride interfered in the detection of hypochlorite.

Starobinets and Mechkovskii[19] found that perchlorate could be separated from chloride and chlorate ions by partition chromatography on a cation-exchange resin using aqueous acetone as eluent.

The separation of chloride, chlorite, chlorate, and perchlorate by ion exchange chromatography has been described by Boyd and Larson.[20] The ions were eluted from Dowex-1, in the order named, using potassium bicarbonate solution for the first three and sodium fluoroborate solution for perchlorate, the most strongly held ion of the four.

Loach[21] took advantage of the strong affinity of perchlorate ion for ion exchange resins of the quaternary ammonium type to isolate and concentrate perchlorate ions from plant and animal extracts. Perchlorate was recovered from the columns, after washing with water, by elution with 1 *M* ammonium trichloroacetate.

The chromatographic behaviors of halate and perhalate ions on strong-base anion exchange resin paper (nitrate ion form) have been described by Lederer and Sinibaldi.[22] Their study also included evaluation of the properties of the same anions in paper electrophoresis and in thin-layer partition chromatography. They concluded that many different separations of one ion from others were practical by the different methods.

Extration of perchlorate ions from aqueous solution into a liquid anion exchanger or into an immiscible solvent in the form of an ion- association complex can serve as a means of minimizing interferences as well as for converting the perchlorate into a measurable form. Although numerous extraction systems have been investigated, none provide as high a degree of separation specificity as that afforded by the chromatographic methods just described. The following liquid anion exchangers are typical of those that have been evaluated for perchlorate extractions: Amberlite LA-2 liquid resin (a long-chain aliphatic amine),[23] tetrahexylammonium picrate in methylene chloride,[24] and trilaurylamine in various water-immiscible solvents.[25] Of the many different extractable ion-association complexes that have been utilized in perchlorate separations, the following are typical: tetrabutylphosphonium perchlorate,[26] tris(1,10-phenanthroline)zinc(II) perchlorate,[27] and dimethyldiaminophenazine perchlorate.[28]

The extraction of perchloric acid and other strong monobasic mineral acids by organic bases dissolved in water-immiscible solvents has been extensively investigated. Amines studied as extractants include tri-n-octylamine,[29-31] hexadecylamine,[32] and di-2-ethylhexylamine.[33] Extraction by trioctylamine increases in the order $HCl < HBr < HNO_3, < HClO_4$. Extractants studied of the organophosphorus type include tributyl phosphate,[34,35] trioctylphosphine oxide,[36-38] and diethyl(N,N-dibutylcarbamoyl)phosphonate.[39] Other extractants investigated include di(n-octyl)arsenic acid,[40] tris(n-octyl)arsine oxide,[41] di-n-heptyl sulfoxide,[42] and nitrobenzene,[43] For acid concentrations less than 4 N, the order of extractability from aqueous solution by 1 M di-n-heptyl sulfoxide in trichloroethane solution was $HNO_3 > HClO_4 >> HCl \approx H_2SO_4$.

Reduction of Perchlorates

Various methods have been described for the reduction of perchlorates as a means for either their direct determination by titrimetric redox methods or their indirect determination by gravimetric or titrimetric determination of the liberated chloride. The reduction methods are of three types: thermal decomposition, wet chemical, and electrochemical. With few exceptions, they require the use of appropriate catalyst or high temperature in order to be practical for analytical purposes.

Although perchlorates can be decomposed simply by heating at sufficiently high temperatures, it is more common and prudent to decompose them by fusion with other substances or by cautiously heating their mixtures with suitable reductants. Lamb and Marden[44] employed fusion with sodium carbonate in glass test tubes to reduce perchlorates to chloride prior to gravimetric determination of the resulting chloride. Loss of chloride was prevented by the use of two plugs of asbestos wool inserted in the test tubes, one near the top and the other in the middle. Lenher and Tosterud[45] found that they could reduce perchlorates rapidly by heating the samples in a porcelain crucible in the presence of manganese dioxide at 600 to 700°; however, they recommended that the method of Lamb and Marden be used for greater accuracy. Dobroserdov and Erdmann[46] reported obtaining high accuracy with the Lamb and Marden method, provided that the heating was carried out in hard glass tubes and not too intensely nor prolonged. Reduction of perchlorates to chlorides can be accomplished rapidly by fusion with either sodium nitrate in a nickel crucible[47] or with sodium peroxide in a Parr bomb.[48] Meldrum and coworkers[49] employed a stainless steel bomb to explosively decompose perchlorate in smokeless powder prior to determining the resulting chloride by the Volhard method. Scharrer[50] reduced perchlorate to chloride by heating with copper powder in a covered crucible. Sodium oxalate has also been employed as a reductant in thermal decomposition of perchlorate to chloride.[51]

Numerous wet chemical methods for the reduction of perchlorate to chlorine or to chloride have been described. Reduction with titanium(II) has been most extensively studied, first by Rothmund[52] in 1909, then by Meldrum and coworkers,[49] followed by Burns and Muraca.[53] The latter employed osmium tetroxide as a catalyst for the reduction of perchlorate to chloride by titanous chloride. Back-titration of excess titanium(II) with standard iron(III) served to determine the perchlorate. Use of oxygen-free or inert atmospheres is necessary to avoid air oxidation of titanium. Others who have employed titanium(II) as a reductant for perchlorate include Vil'yamovich,[54] Peebles,[55] Schnell,[56] Eagles,[57] and Huskens and Gaty.[58] Reduction of perchlorate with ferrous oxide in sodium hydroxide was studied by Sjollema,[59] with starch in concentrated sulfuric acid by Willard and Thompson,[60] and with sulfur in sulfuric acid by Durand.[61] Molybdenum catalysis of the reduction of perchlorate to chloride ions by stannous salts or zinc metal has been studied extensively by Haight,[62] who concluded that molybdenum(IV) was the only catalytic species. Laitinen and Rechnitz[63] quantitatively reduced perchlorate to chloride with liquid cadmium amalgam in the presence of sodium molybdate catalyst. Crowell and coworkers[64,65] found that osmium(IV) and ruthenium(III) ions exert catalytic effects on the reduction of perchloric acid by hydrobromic acid in dilute solutions at room temperature and at 100°. The redox reaction was stoichiometric, yielding chloride ions and bromine. Tungsten carbide was found to catalyze the reduction of perchlorate ions by molecular hydrogen.[66]

Electrochemical reduction of perchlorate to chloride ions can be accomplished in concentrated sulfuric acid and in mixtures of sulfuric and nitric acid; however, considerable time is required for quantitative reduction.[67] At a mercury cathode the reduction is much more rapid when catalyzed by the presence of molybdenum(IV). Rechnitz and Laitinen[68] found that molybdenum(IV) was reduced by a molybdenum(V) dimer which was then reoxidized by perchlorate. Polarographic studies by Haight[62] indicated that molybdenum(IV) was the active catalytic species. The reduction of perchlorate to chloride ions at tungsten carbide electrodes by electrochemically generated molecular hydrogen was reported by Vertes and Horanyi.[69]

Determination of Perchlorate

To assure reliability of results the determination of perchlorate in complex mixtures should involve some prior separation procedure. None of the chemical reactions upon which the measurements are based possess sufficient selectivity to be free of interferences. The most direct, and perhaps the most reliable, determinations are those that are based upon precipitation of perchlorate as an insoluble salt. Precipitation can be monitored by radiometric or spectrophotometric means or measured gravimetrically or titrimetrically. Methods based upon the determination of either the reduction products of perchlorate (chloride or chlorine) or the excess reducing agent after reduction of perchlorate are indirect and more susceptible to error and interferences.

Photometric methods for perchlorate are commonly based upon precipitation or extraction of perchlorate ions in association with a colored cationic species, followed by measurement of the absorbance due to either the cationic species combined with the perchlorate ion in the new phase or that remaining in excess in the original phase. These indirect methods, although very sensitive, are highly subject to interferences. Under optimum conditions, the relative random error involved in photometric determination of perchlorate may be 1 to 2%.

In the absence of interferences, perchlorate ion concentration can be estimated most rapidly by potentiometry with appropriate ion-selective electrodes. Relative errors, depending on concentration levels, are commonly in the 1 to 10% range.

Gravimetric methods. At one time perchlorate was commonly precipitated as potassium perchlorate for gravimetric purposes, even though addition of a large amount of ethanol was necessary to minimize solubility losses.[70-73] Quantitative precipitation of perchlorate now can be achieved most effectively through use of certain organic precipitants, notably those which possess or give rise to large bulky cations. Nitron, as described by Storm,[74] was one of the first of such reagents to be employed. It has been used by various investigators as a gravimetric reagent for perchlorate,[75-79] however its solutions are relatively unstable and nitrate interferes.[80]

The tetraphenyl derivatives of trivalent phosphorus, arsenic, and antimony salts have been found to be practical gravimetric reagents for the determination of perchlorate. Investigations by Willard and coworkers[81,82] have demonstrated that a large number of different anions are quantitatively precipitated by these reagents. Of the three, tetraphenylarsonium chloride forms a more insoluble perchlorate than either tetraphenylphosphonium[83] or tetraphenylstibonium chloride,[84] and thus is the most commonly used. According to Loach[85] a 1 *M* sodium chloride medium provides desireable influences on the solubility and filterability of tetraphenylarsonium perchlorate precipitates. Gravimetric procedures for perchlorate using tetraphenylarsonium chloride have been described by various workers.[81,83,86-88] Use of tetraphenylphosphonium chloride for the gravimetric determination of perchlorate in the presence of nitrate[89] and in the presence of chlorate ions[90] has also been described.

Tetra-n-pentylammonium bromide has proven to be a suitable gravimetric reagent for the determination of perchlorate in amounts ranging from 2 to 50 mg.[91] Equivalent amounts of chlorate do not interfere. Interference from larger amounts of chlorate can be eliminated by prior reduction with sodium bisulfite, an excess of which is without interference.

Various other organic compounds have been proposed or utilized as perchlorate anion precipitants for gravimetry. These include methylene blue,[92,93] α-phenyl-β-diethylaminoethyl-p-nitrobenzoate,[94] 1,2,4,6-tetraphenylpyridinium acetate,[95] and 3,5,6,8-tetramethyl-1,10-phenanthroline.[96]

Gravimetric determination of perchlorate can also be effected indirectly after reduction of chloride by appropriate methods. Lamb and Marden[44] employed decomposition by sodium carbonate fusion followed by precipitation of chloride as silver chloride for the gravimetric determination of various perchlorate compounds. Dobroserdov and Erdman[46] reported obtaining satisfactory results by the same procedure. Willard and Thompson[60] employed starch and a concentrated solution of sulfuric acid for the reduction, distillation for the separation of the resulting hydrochloric acid, and precipitation with silver nitrate to determine perchlorate indirectly. Various other methods for the reduction of perchlorates prior to gravimetric determination of the resulting chloride are cited in the previous section.

Titrimetric methods. Potentiometric,[97-99] thermometric,[100] and conductometric[101] methods have been described for the precipitation titration of millimolar amounts of perchlorate with tetraphenylarsonium chloride. Various interferences are commonly encountered, especially by large and symmetrical anions.

An amperometric titration procedure based on tetraphenylstibonium sulfate as the precipitation titrant for perchlorate has been described by Morris.[84] Contrary to many classical titrimetric procedures for perchlorate, the method is claimed to be free of interferences from chloride, chlorate, nitrate, phosphate, and sulfate.

Bolliger[102] reported determination of as little as 1 mg of perchlorate by treatment with a measured amount of methylene blue, removal of the precipitate by filtration, and titration of the excess methylene blue with picric acid.

Willard and Smith[81] determined perchlorate iodometrically by precipitation as tetraphenylarsonium perchlorate followed by titration with standard iodine.

Several back-titration methods based upon the reduction of perchlorate followed by titrimetric determination of the excess reductant have proven satisfactory for the determination of perchlorates. Burns and Muraca[53] employed titanous chloride as reductant, osmium tetroxide as catalyst, and standard ferric ammonium sulfate for back titrating the excess titanium(III) reductant. A similar procedure was described by Meldrum and coworkers.[49] Aravamudan and Krishnan[103] found that iron(II) can quantitatively reduce perchlorate to chloride if sufficiently high temperature and concentrated sulfuric acid are employed. They determined perchlorate by reduction of the perchlorate with ferrous sulfate in 11 to 12 *M* sulfuric acid at 150 to 155° for about 15 min., followed by back-titration of the excess iron(II) with standard permanganate after cooling and dilution with water. Nitrate interference could be corrected for by a separate determination under milder conditions such that only nitrate was reduced by iron(II).

Numerous methods have been described for the determination of perchlorate based upon the titration of chloride obtained on reduction of the perchlorate. They differ in choice of reductant or decomposition method and in chloride ion precipitation technique. Sjollema[59] employed reduction by iron(II) in sodium hydroxide followed by the Volhard method for chloride. Kurz, Kober, and Berl[104] fused the perchlorate with an excess of sodium nitrite at 500° for 1.5 hr. to obtain chloride which was subsequently determined by the Volhard or the potentiometric method. A similar reduction method was employed by Yamasaki and coworkers[47] to determine perchlorate in a mixture of chloride, hypochlorite, chlorite, chlorate, and perchlorate. Chloride before and after reduction was determiend by amperometric titration with standard silver nitrate. Fusion with sodium peroxide and potassium superoxide followed by the Volhard method was used by Riolo and Occhipinti[105] to analyze mixtures of perchlorates and chlorates. Reduction of perchlorate was complete only in the presence of organic matter. Simonyi and Tokar[106] employed reduction with Raney nickel alloy in boiling, dilute sodium hydroxide to reduce chlorate without interference from perchlorate. For the reduction of both chlorate and perchlorate they fused the sample with potassium hydroxide in the presence of ethyl alcohol. Chloride was determined by the Volhard method, and the difference in amounts of chloride produced by the two reduction methods enabled calculation of the perchlorate content of the sample. Alley and Dykes[107] determined perchlorates in pyrotechnics by reduction with titanium hydride in sulfuric acid followed by potentiometric titration of the resulting chloride with silver nitrate. Matrixes impenetrable by 1:3 sulfuric acid and the presence of cellulose nitrate interfered. The oxygen flask method was used by Secor, Ricci, and White[108] to decompose organic and inorganic samples for the microdetermination of perchlorate, yielding chloride which was titrated coulometrically.

A simple and accurate method for the determination of perchlorate in mixtures of other chlorine-containing components consists of the total decomposition of one portion of sample to chloride by ignition with ammonium chloride and the selective reduction of another portion such that all chlorine-containing components except perchlorate are converted to chlorides. The difference in chloride content obtained by the two methods represents chloride obtained from perchlorates, from which the perchlorate concentration is determined. Procedures based on this method have been described by Scott[109] and others.[47,106,110,111]

Titration of perchloric acid. Determination of perchloric acid with standard base requires special techniques if the sample contains other acids or metal ions that interfere through formation of stable hydroxy species. Mixtures of perchloric and nitric acids have been differentiated by potentiometric titration with potassium hydroxide using ethyl methyl ketone as solvent.[112] Perchloric acid has also been determined without interference from nitric acid by a high frequency titration method using a solvent medium of acetic acid and a titrant of diphenylguanadine or pyridine in acetic acid.[113] Sansoni[114] reported obtaining 6 distinct and points in the conductometric titration of a mixture of perchloric, p-methylsulfonic, sulfuric, nitric, and trichloroacetic acids in a solution of acetic acid containing 1% water using 0.5 M sodium acetate as titrant.

Potentiometric titration of aqueous mixtures of perchloric and acetic acids with sodium hydroxide yields two breaks; however, the first is rather poorly defined and limits the precision of the perchloric acid determination. If the solution is diluted with an equal volume of dioxane prior to the titration, the sharpness of the first inflection or break is considerably enhanced, permitting much improved accuracy in the differentiation and determination of the individual acids.[115]

The determination of perchloric acid in cotton acetylation bath solutions has been described by Buras, Cooper, and Cruz.[116] Containing either acetic acid - acetic anhydride -

perchloric acid or acetic acid - water - perchloric acid, the three-component baths were analyzed for perchloric acid content by titration with standard potassium biphthalate after dilution with a mixture of acetic anhydride and acetic acid to assure that any water present was consumed by the acetic anhydride. p-Naphtholbezein was used as indicator.

Certain metal perchlorates have been analyzed by electrodeposition of their aqueous solutions followed by titration with standard base of the metal-free perchloric acid solution that results from the electrolysis. This unique method yields the metal content by electrogravimetry and the perchlorate content by acidimetry. It has been applied with varying degrees of success to the analysis of the perchlorates of cobalt,[117] nickel,[117] iron,[118] and lead.[75] Interference from anions other than perchlorate and incompleteness of electrodeposition constitute rather serious limitations for the method.

Photometric methods. Most of the photometric methods for perchlorate are indirect, involving spectral measurements either in the visible or ultraviolet region of the absorbance due to cationic species in association with the sought-for perchlorate after some suitable ion-association reaction or separation. The only direct photometric methods are those based upon measurement of the characteristic infrared absorption of perchlorate ions.

For the determination of perchlorate by infrared spectrophotometry it is necessary to separate the perchlorate anion from other strongly absorbing components in the sample. Aqueous samples can be evaporated to dryness or extracted with a suitable non-polar solvent, one which is relatively non-absorbing in the infrared region of interest. Such procedures, although time consuming, also serve to concentrate the perchlorate and thus enhance the sensitivity of the determination. Solid samples are prepared for spectral measurement in the form of pressed disks, either as obtained or mixed with potassium bromide. Absorbance measurements are made at a wavelength corresponding to the maximum of any one of the three intense, broad bands due to perchlorate in the 8.5 to 10 μm (1000 to 1150 cm^{-1}) region.

Loach[21] devised a sensitive and highly selective method for the determination of trace amounts of perchlorate in plant and animal tissues utilizing infrared spectrophotometry for the final measurement step. Organic samples were chopped into small pieces and boiled with distilled water to extract the perchlorate content. After filtration, clarification, and concentration of the filtrate by evaporation, the perchlorate was taken up on a column of Dowex 2-X8 ion exchange resin in the trichloroacetate form. After washing, the perchlorate was eluted from the column with 1 M ammonium trichloroacetate and precipitated by addition of tetraphenylarsonium chloride solution and potassium perrhenate solution. Complete recovery of the perchlorate was achieved by its coprecipitation with the tetraphenylarsonium perrhenate. The precipitate was collected, dried in vacuo, ground with potassium bromide, pressed into a disk, and its infrared spectrum recorded. The following results for 2-kg samples were typical, with concentrations expressed as μg $KClO_4$ per kg of sample: sea water, 0; silver beet, 9-12; urine, 21-28; and cabbage, 9.

Briggs and coworkers[119] employed infrared spectrophotometry to determine potassium perchlorate in potassium chlorate. To avoid the risk of explosion when compressing samples into transparent disks, the samples were first boiled with hydrochloric acid to decompose the chlorate and then evaporated to dryness. A relative standard deviation of 5% for 0.3% $KClO_4$ was found for the method.

Dolinski and Wilson[23] determined perchloric acid in the presence of nitric, sulfuric, and chloric acids by extracting the aqueous solution with a carbon disulfide solution of Amberlite LA-2 liquid resin followed by infrared spectrophotometric analysis of the extract. The absorbance of perchloric acid in the extracts, followed Beer's law up to a concentration of 3 mg/ml.

Many indirect photometric methods are based upon liquid-liquid extraction of perchlorate in the form of an ion-association complex with a suitably absorbing cationic species or dye. Measurement of the absorbance of the extracted dye-perchlorate complex thus provides an empirical basis for determining the perchlorate. In general, these methods provide high sensitivity but low selectivity. One of the more commonly employed methods[120] of this type uses methylene blue as the cationic species and chloroform as the extracting solvent. The methylene blue-perchlorate complex in chloroform obeys Beer's law at 655 nm for perchlorate concentrations up to 0.5 ppm. A similar method, using 1,2-dichloroethane and extraction from an acidified solution rather than from pH 5-7, was described by Iwasaki and coworkers.[121] Interferences from many different anions and certain cations can be minimized by masking with mercuric ions or by an aqueous sulfuric acid backwash. Applied to the determination of perchlorate in sea water samples, the method indicated that perchlorate was either absent or less than 0.05 ppm.

Various workers[122-126] have investigated brillant green for the extraction-photometric determination of trace amounts of perchlorate. The ion-association complex is extracted from aqueous solution of pH 4-7 into benzene where its molar absorptivity is 9.4×10^4 at 640 nm.[123,124] Nile blue[127] and neutral red[28] have also been studied as extraction-photometric reagents for perchlorate. The molar absorptivity of the neutral red-perchlorate in nitrobenzene is 9.39×10^4, and that of the nile blue complex in 1,2-dichlorobenzene is 8.1×10^4 at 650 nm.

Certain complex metal cations have proven to be sensitive extraction-photometric reagents for the indirect determination of microamounts of perchlorate. The ion association complex of ferroin perchlorate has been extracted into n-propylnitrile[128] and into nitrobenzene[129] to determine perchlorate at the ppm-level. Similarly, the extraction of neocuproine copper(I)-perchlorate into ethyl acetate has served as the basis for the indirect determination of perchlorate concentrations from 0.5 to 5.0 ppm.[130,131] The perchlorate salt of the copper(I) complex of 6-methylpicolinaldehyde azine is extractable into either chloroform or isobutyl methyl ketone, enabling determination of perchlorate indirectly by measurement of the absorbance of 480 nm, with a relative error of ±1.3% at a level of 12 ppm.[132]

For the determination of perchlorate in potassium chlorate Fogg and coworkers[26] extracted the perchlorate into o-dichlorobenzene in the form of its ion association complex with tetrabutylphosphonium ion. On washing the organic extract with an aqueous solution of ferric thiocyanate, the perchlorate ion was replaced yielding a colored iron(III)-thiocyanate, tetrabutylphosphonium complex for which an absorbance measurement at 510 nm proved proportional to the original perchlorate ion concentration. Beer's law was followed up to 500 μg of perchlorate. Interferences from iodide, nitrate, chlorate, and bromide were eliminated by evaporating the sample to dryness, first from hydrochloric acid and then water solution before analysis.

Irving and Damodaran[133] determined perchlorate in the presence of other halogen species in aqueous solution by means of a colored liquid anion exchanger, a solution of tetrahexylammonium tetranitritodiamminocobaltate(III) in xylene and iso-butyl methyl ketone. The cobaltate complex anion exchanged quantitatively with perchlorate and was determined photometrically by the increase in absorbance in the aqueous solution or by the decrease in the absorbance in the organic phase at 353 nm. Interferences by chlorate, hypochlorite, chlorite, nitrite, and nitrate were eliminated by fuming the samples with hydrochloric acid. A similar indirect photometric method for perchlorate, using tetrahexylammonium picrate as the liquid anion exchanger, was described by Gustavi and Kylberg.[24]

Precipitation of perchlorate with a measured quantity of a colored precipitant followed by filtration and photometric determination of the excess is a general indirect method for perchlorate that has been employed by a number of investigators. Nabor and Rammachandran[134] used methylene blue as the precipitant. A correction was necessary for the solubility of the precipitate. To determine perchlorate in blood Kurz and Renner[135] precipitated the perchlorate with nitron and determined the excess nitron by its absorbance at 490 nm in alcoholic sodium hydroxide solution. Shahine and Khamis[136] also used nitron for precipitation of perchlorate; however, they determined the excess by extraction with a cobalt thiocyanate complex anion into cyclohexane-carbon tetrachloride and photometric determination of the absorbance of the complex at 625 nm. Excess nitron, after precipitation of perchlorate, has also been determined by an iodometric procedure.[137]

A simple indirect method which involves neither precipitation nor extraction was devised by Trautwein and Guyon.[138] Based upon the quantitative interference of perchlorate in the spectrophotometric determination of rhenium with α-

furildrioxime, their method proved capable of a sensitivity comparable to that of the ferroin method.[128] Interference, however, was quantitative for the following ions: $S_2O_3^{-2}$, Cu^{+2}, V^{+5}, NO_3^-, NO_2^-, and UO_2^+.

Ion-selective electrodes. In recent years a variety of membrane type electrodes have been developed that exhibit highly selective, Nernstian response toward perchlorate ion activities. Most perchlorate ion selective electrodes are of the liquid-membrane type, although a few precipitate-type (heterogeneous) and at least one solid state type have been devised. Details of the theory and technology of ion selective electrodes in general have been extensively reviewed.[139-142] The most significant advantages afforded by ion selective electrodes are simplicity and speed of application for measurement or monitoring of individual ion activities. However, a number of limitations and precautions should be recognized in their use: (1) they are not specific, only selective towards a particular ion or group of ions, so interferences are common; (2) they measure activities not concentration of ionized species, thus complexation and ionic strength influence the results; and (3) their response frequently depends upon pH, age, condition, temperature, and time. For direct concentration determination their use requires empirical calibration curves, frequent standardization, and reliable standard solutions. However, for use as indicating electrodes in potentiometric precipitation or complexation titrations these factors are no longer important. Ion selective electrodes are ideally suited for following concentration changes in chemical processes, reations, kinetics, and titrations.

One of the most extensively studied and widely used perchlorate ion electrode is the commercially available Orion Model 92-81 electrode. This liquid-membrane type electrode has a useful linear response to perchlorate ion over the molar concentration range of 10^{-1} to $10^{-3.5}$ in aqueous systems of pH to 11. It exhibits reasonable selectivity for perchlorate over common anions such as nitrate, bicarbonate, and the halides.[143,144] Its response time increases with decreasing perchlorate ion concentration, requiring at least 15 sec. to attain a constant reading for 10^{-5} molar solutions.[145] In addition to direct determination of perchlorate ion concentration, the Orion perchlorate electrode has found use in determination of solubility products of slightly soluble perchlorates[144] and in potentiometric titrations[145] It has also proven useful for the determination of vicinal glycols by an automatic reaction rate method[146] and for catalytic titrations involving periodate indicator reactions.[147]

Various liquid membrane electrodes have been studied that are similar to the Orion perchlorate electrode in construction and composition. Ishibashi and Kohara[148] reported that a nitrobenzene membrane containing bathoferroin perchlorate showed excellent selectivity for perchlorate over nitrate or iodide and gave linear Nernstian response up to about 10^{-5} M perchlorate. Reinsfelder and Schultz[149] determined selectivity coefficients for common inorganic ions of electrodes of the liquid membrane type containing tris(1, 10-phenanthroline)iron(II) in nitrobenzene and tris(4,7-diphenyl-1-,10-phenanthroline)iron(II) in nitrobenzene, chloroform, or n-amyl alcohol. Selectivity coefficients were relatively independent of membrane composition with a sequence of selectivity as follows: $PF_6^- > ClO_4^- > SCN^- \sim I^- \sim BF_4^- > NO_3^- > Br^- > Cl^-$. *Rohm and Guilbault*[150] *prepared a mixture of* polyvinylchloride and the commercially available liquid exchanger from the Orion perchlorate electrode to construct disks and coated-wire electrodes which proved similar in response to the Orion electrode. The construction and characterization of liquid-membrane electrodes containing the perchlorate salt of tris(1,10-phenanthroline)iron(II) and that of the analogous nickel(II) chelate in nitrobenzene have been reviewed by Hopirtean *et al.*[151]

A liquid membrane type electrode based on the perchlorate salt of tetrakistriphenylphosphinesilver(I) has been claimed to be superior to the Orion perchlorate electrode with respect to applicability to basic solutions.[152]

Coetzee and Freiser[153,154] found that methyl tricapryl ammonium salts (Aliquat 336S) in 1-decanol function effectively as organic phase components in liquid-liquid membrane electrodes for the determination of a variety of anions. The perchlorate electrode of this type exhibited linear potential response over the concentration range 10^{-1} to 10^{-3} M perchlorate. Tateda, Fritz, and Itani[155] reported that electrodes prepared using Aliquat 336 proved less favorable than the commercially available (Orion) perchlorate electrode. Other quaternary ammonium perchlorates have been explored extensively as ion-exchangers for use in liquid membrane electrodes in attempts to develop improved perchlorate electrodes. These studies have produced practical but not superior electrodes. Systems studied, in addition to Aliquat 336, include methylcetylbenzylammonium salts in nitrobenzene fixed on charcoal or graphite,[156] tetraalkylammonium salts in ethyl bromide,[157,158] tetraoctylammonium perchlorate in toluene,[159] and octadecyldimethylbenzylammonium perchlorate in nitrobenzene.[160] Quaternary phosphonium salts have also been investigated for use in perchlorate selective membrane electrodes.[161]

A perchlorate ion-selective electrode based upon a liquid membrane consisting of methylene blue perchlorate in nitrobenzene has been reported to exhibit Nernstian response towards perchlorate over the range 10^{-6} to 1 M perchlorate, independent of pH over the range 2 to 12.5.[162] Similar results were found for the electrode based on the tetrafluoroborate salt of methylene blue in tetrachloroethane.[163] Brilliant green perchlorate, another basic dye salt, has been examined as an ion-exchanger for liquid membrane electrodes.[164] A chlorobenzene solution of this salt in natural rubber served as the membrane for an electrode that gave a useful linear response over the 0.1 to 0.001 M perchlorate range for solutions of pH 4 to 8.[165]

An exceptionally sensitive perchlorate electrode has been described by Sharp.[166] Containing a liquid membrane prepared from a solution of N-ethylbenzothiazole-2,2'-azaviolene perchlorate in 1,2-dichlorobenzene, the electrode exhibited a response range of 1 to $10^{-6.5}$ M perchlorate, a useful pH range from 1 to 12, and high selectivity for perchlorate over all of the 10 anions tested. A solid-state electrode made from the same radical ion salt has also been described by Sharp,[167] but its selectivity and response characteristics are less favorable.

Several moderately sensitive perchlorate electrodes of the heterogeneous (precipitate) type have been described that possess the advantage of simplicity of fabrication. James and Freiser[168] prepared such an electrode by coating platinum wire with a mixture of polyvinylchloride and the ion-association complex between Aliquat 336S (a quaternary ammonium cation) and perchlorate. Hiro, Tenaka, and Kawahara[196] coated graphite with a suspension of cadmium perchlorate in Urushi (a natural lacquer). Ishibashi and coworkers[170] impregnated *tetradecyldimethylammonium perchlorate in a plastic* matrix to construct an electrode that exhibited linear response down to 10^{-3} — 10^{-4} M perchlorate.

Miscellaneous methods. *The radiochemical method of* isotopic dilution, using chlorine-36 labeled potassium perchlorate, was employed by Johannesson[171] to investigate the question of the occurence of perchlorate in natural sea water. None was found within the limits of sensitivity and accuracy of the method (± 4.2 mg $KClO_4$ per 250ml, for the 95% confidence limits).

An indirect radiometric procedure for the determination of perchlorate after extraction as an ion association complex with radioactive zinc complexed with 1,10-phenanthroline has been described by Shigematsu *et al.*[27] Extracted into a measured volume of nitrobenzene from pH 7 aqueous solution, the activity of zinc-65 is measured by a scintillation counter and is proportional to the amount of perchlorate ion in the original sample. For 10-ml samples a concentration range for perchlorate of 2×10^{-7} to 10^{-6} M is suitable for analytical purposes. Many different anions interfere but not chloride, sulfate, or phosphate.

Bishop and Evans[172] devised a rate-measurement method *for the determination of perchlorate at low concentrations* based on the homogeneous reaction kinetics of titanium(III) with perchlorate.

Mixtures of chloride, chlorate, and perchlorate were analyzed by Gnanasekeran *et al.*[173] by ion-exchange chromatography. The anions were collected on a column of a special resin (developed from cashew nut shell liquor, treated with hydrochloric acid, and washed with water), eluted in their acid form with water, and titrated with standard sodium hydroxide. Replicate determinations agreed to within ± 1%.

Analysis of Perchlorate Compounds and Mixtures

Specifications and procedures for testing the quality of sodium, potassium, and magnesium perchlorates and of 70% perchloric acid as reagents have been compiled by Rosin.[174] Requirements for ACS reagent grade specification and test procedures have been established for lithium perchlorate[175] and for potassium and magnesium perchlorates as well as for

60% and 70% perchloric acid solutions.[176] Procedural details include assay of the perchlorate, determination of residue on ignition, insoluble matter, chloride, chlorate, nitrate, sulfate, calcium, heavy metals (as lead), and iron.

A rapid method for checking the concentration of perchloric acid solutions (from 0 to 72% by weight) has been described by McLean and Pearson[177] based on measurement of refractive index. Smith and Lamplough[178] proposed the same procedure, however the accuracy of their data was questioned by McLean and Pearson. Refractive indices at 20° and 30° are compiled in Table 8 (in Chapter II) as a function of concentration. Density determinations have also been advocated for checking perchloric acid concentrations.[179]

Elemental analysis of organometallic perchlorates for carbon, hydrogen, and nitrogen involves considerable risk of explosion when the samples are ignited. It has been reported that explosive compounds can be safely analyzed by first mixing the perchlorate sample with cobalt oxide and/or copper oxide prior to heating in the combustion furnace. A disadvantage of the method, however, is that nitrogen values tend to be about 0.2 to 0.3% low.[180]

Trace metal determinations by atomic absorption spectrophotometry are subject to interference from perchloric acid. Oguro[181] found that perchloric acid (0.001-0.10 M) enhanced the absorption of Mg, Ca, Mo, Cr, and V and decreased the absorption of Fe, Ni, and Co in an air-acetylene flame. Others have reported perchloric acid interference in flameless atomic absorption spectroscopy also.[182,183] Thus in the analysis of perchlorates and perchloric acid solutions for trace metal content, it is imperative that standard solutions used in preparing calibration curves be of the same perchlorate composition as the unknown if reliable results are to be obtained.

Other than the above, relatively few procedures have been published for analysis of impurities in perchlorates. A method for the determination of free acid in aqueous solutions of uranium(IV) perchlorate has been described by Schmid and Junger.[184] Several papers by Russian chemists on the determination of titanium in perchloric acid and perchlorate salts have been cited by title in Chemical Abstracts.[185-187]

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CHAPTER VII

BIOLOGICAL EFFECTS OF PERCHLORATES

Although ammonium, potassium, and sodium perchloates exert a number of interesting biological effects in both plants and animals, their toxicities are relatively slight. Nothing in the long history of their manufacture points to any appreciable biological hazard for a worker exposed to them for prolonged periods. According to Levens,[1] who critically review the literature prior to 1960 on the biological action of perchlorates, sodium and potassium perchlorates would be considered to be "slightly toxic" to animals under the classification scheme of Hodge and Sterner.[2] Several other perchlorates, however, are known to be more than slightly toxic. Still others, the great majority, remain to be investigated. In fact, much remains to be learned about the biological modes of action of even the sodium and potassium perchlorates.

ANIMAL STUDIES

Physiological Effects

The effects of perchlorate ions on the thyroid gland and its function in various animals have been extensively investigated. Wyngaarden *et al.*[3] found that perchlorate produced quantitative discharge of iodide from rat thyroids within 15 min. It proved to be about 10 times more effective than thiocyanate and approximately 300 times more than nitrate. The blocking effect of perchlorate on the collection and retention of iodide by the thyroid may also extend to other iodide-concentrating mechanisms of the animal body.[4] Rats treated with perchlorate for 17 days developed goiters which were hyperplastic and low in iodine.[3] Wyngaarden and coworkers[5] also observed that increasing amounts of iodide, thiocyanate, perchlorate, and nitrate produced marked reductions in the ability of the thyroid glands of rats to concentrate radioiodide. Perchlorate proved to be the most potent anion and nitrate the least. Halmi and Stuelke[6] found that subcutaneous injection of 100 mg or more of sodium perchlorate prevented active uptake of iodine-131 by thyroid glands of rats treated with propythiouracil, a substance known to prevent hormone synthesis involving the combination of tyrosyl groups and iodide ions. According to Krúskemper and Kleinsorg,[7,8] potassium perchlorate interferes with the synthesis of thyroxine in rats and mice. Results obtained by Breslavskii and Simon[9] appear to support this opinion, although contradictory to the conclusions of Wyngaarden and coworkers.[3]

Kleinsorg and Krúskemper[10] studied the effects of thyroxine and antithyroid substances (potassium perchlorate and methylthiouracil) on the serum proteins in rats. Potassium perchlorate fed simultaneously with thyroxine prevented decreases in serum protein. When fed alone at 100 or 250 mg/kg/day, potassium perchlorate raised the β-globulin content by 68 percent in 14 days and 94 percent in 28 days, while the albumin/globulin ratio was lowered from 1.8 to 1.17.

Selivanova[11] found that ammonium perchlorate is as potent as either sodium or potassium perchlorate for inhibiting thyroid accumulation of iodine-131 in rats, mice, and rabbits. Tests with $NH_4{}^{36}ClO_4$ revealed no cumulative toxicity for dogs. Mice gained weight on an ammonium perchlorate treatment of less than 260 mg/kg and lost weight at greater doses.

Kinetics of the distribution of radioactive perchlorate in rat and guinea pig thyroid glands have been studied by Chow and Woodbury.[12] A kinetic analysis of iodide transport in dog thyroid slices by Rochman *et al.*[13] indicated that 1 m *M* sodium perchlorate solution inhibited the influx of iodide into the follicles and discharged the trapped iodine-131 into the media with an increased efflux rate.

Mikhailov[14] found that sheep which received 100 mg of ammonium perchlorate per kg weight or 2 mg/kg/day for 6 months with their feed showed decreased protein-bound iodide in the blood, decreased inorganic blood iodide, and increased urinary and fecal iodide excretion. The compound acted directly on the thyroid gland to alter its function. Yamada and Nakamura[15] observed that perchlorate exerts a contracting effect on thyroid glands.

Rousset, Orgiazzi, and Mornex[16] reported that perchlorate ions enhanced thyroid responsiveness in mice to thyrotropin, human chorionic gonadtropin, and long active thyroid stimulators.

Harden and coworkers[17,18] found that perchlorate ions exert an inhibitory effect on the parotid saliva gland. After administration of perchlorate the labial saliva/plasma ratio for iodine-131 decreased 47 per cent from the control value.

Nevelichuk[19] observed antiarrhythmic properties for potassium perchlorate. Given orally to rats each day for 3 days, potassium perchlorate (20 to 910 mg/kg) prevented ventricular fibrillation induced by calcium chloride (i.v.) and decreased the cardiotoxic action of calcium chloride. No relationship between the antiarrhythmic effect and antithyroidal activity was found.

The use of perchlorate as weight stimulators for poultry and farm animals is discussed in Chapter V.

Perchlorate Metabolism

Various studies indicate that perchlorate salts are eliminated in the urine by most animals without chemical reduction of the perchlorate ion. Kerry and Rost[20] recovered perchlorate unchanged in the urine of rabbits administered sodium perchlorate intravenously. Rabuteau[21] recovered potassium perchlorate unchanged in urine of patients treated for malaria. Quantitative recovery of sodium perchlorate from a human subject was reported by Durand.[22] Appearance of sodium perchlorate in urine occured 10 min. after injection. Maximum concentration was observed at about the third hour, and 95 per cent elimination had occured after 48 hr. Eichler[23] observed similar results for the elimination of potassium perchlorate taken orally by man.

Durand[22] discovered sodium perchlorate distributed throughout the entire rabbit body soon after intravenous or intramuscular injection or oral administration. Determined over the time interval of 20 to 130 min. after administration, concentrations of sodium perchlorate were highest in the ovaries, adrenal glands, and urine. Next highest concentrations were found in the spleen, gall bladder, and intestinal mucosa. Concentrations were lower in the heart, liver, kidneys, lungs, brain, blood, gastric mucosa, muscle, bone and testes.

Eichler and Hackenthal[24] found that perchlorate elimination by rats was faster following high than smaller doses, especially during the early hours after administration. Up to 95 to 97 per cent of the perchlorate was excreted in the urine within 60 hr. In a study of potassium perchlorate metabolism in the rat, Goldman and Stanbury[25] found no *significant concentration of perchlorate in the kidney, liver,* brain, or spleen. They found that the rates of disappearance of the $^{36}ClO_4^-$ radionuclide from the plasma and thyroid and *the rate of appearance in the urine were exponential, with* half-times of approximately 20 hr. These rates are similar to the disposal rates of ^{131}I found by others.

A comparative study of iodine and potassium perchlorate metabolism in the laying hen revealed that the concentration and distribution properties of the two were very similar.[26] It was concluded that perchlorate may be of value in blocking uptake of iodide into eggs.

Pharmacological Studies

The earliest pharmacological study of perchlorates was reported in 1868 by Rabuteau[21] concerning the use of potassium perchlorate as a therapeutic agent against malaria. Some years later Sabbatini[27] completed a comparative study of the pharmacology of oxygenated chlorine compounds in which he found that toxicity generally decreases with decreasing oxidizing properties. The toxicity of perchlorate, however, proved to be an exception to the rule, being less than that of chlorite but more than that of chlorate. Sabbatini attributed the distinctiveness of perchlorate toxicity to an *immobilizaion or diminution effect on potassium ions.*

Pharmacodynamic effects of sodium perchlorate on excised muscles and muscular tissues were investigated by Messini.[28,29] Its addition to the perfusion fluid produced muscle contractions that could be relieved by small amounts of potassium chloride, smaller than that required to inhibit muscle excitability. Washing with sodium chloride enabled the sequence of contraction and relaxation to be repeated. Reversing the order of treatment produced the reverse change, i.e. increased muscle tone from high doses of potassium chloride was diminished by sodium perchlorate. Messini attributed these phenomena to a disturbance of potassium ion equilibrium within the muscle.

From investigations on the reactions of transversely striated muscle (frog sartorius) to sodium and potassium perchlorates and other salts, Boehm[30,31] concluded that the contractions produced by perchlorate and fluoborate anions were both related to precipitation of albumin within the muscle.

Adding to the controversy regarding the cause of muscular contractions induced by perchlorates, Eichler[23] reported that perchlorate-poisoned frog hearts were cured by addition of calcium ion but not by potassium, indicating that *the poisoning was more akin to an excess rather than a* deficiency of potassium. On the other hand, both Cartolari[32] and Spagnol[33] reported pharmacodynamic studies leading to the conclusion that the contraction effect of perchlorate on muscles is produced by decreasing the potassium ion balance.

Hypothyroidism has been successfully controlled in human patients by treatment with oral doses of potassium perchlorate.[34-37] In general, symptoms improved, basal metabolisms fell to nearly normal, body weights increased, and blood cholesterol levels increased to normal values. No significant changes in the formed elements of the blood nor evidence of liver damage were observed for patients treated for as long as 52 weeks.[35]

Brügel[38] found that perchlorate inhibited accumulation of iodine-131 in human subjects to the extent that less than 1 per cent of the normal amount was taken up. According to Lewitus,[39] perchlorate ions compete with inorganic iodide in the trapping mechanism of the thyroid gland, leading to decerased throxine synthesis.

Toxicology and Pathology

Symptoms of perchlorate poisoning in various animals have been described by Kerry and Rost.[20] Frogs injected with 0.015 to 0.030 g of sodium perchlorate exhibited fibrillation, twitching, and strong contraction of transversely striated muscle radiating from the injection site. Reflex excitability was greatly heightened, and heart action was gradually paralyzed. Symptoms were less severe when sodium perchlorate was administered orally, and the frogs recovered completely from oral doses of less than 0.15 g. Similar symptoms (convulsions, paralysis, and rigidity) were observed for sodium perchlorate poisoning in mice, rats, guinea pigs, pigeons, cats, and dogs. Subcutaneous doses of 0.025 g of sodium perchlorate were lethal to mice, 0.22 g to rats, and

1.35 g to guinea pigs. Relatively large oral doses (1 to 2 g) proved fatal to a guinea pig and a rabbit but not to a cat or a dog.

Kahane[40] found that goldfish were unaffected after 3 days in 0.1 per cent sodium perchlorate solution, but that exposure to higher concentrations (0.2 to 2 per cent) resulted in their death. No evidence of reduction of perchlorate to either chlorate or chloride was found.

Leeches immersed in 0.5 per cent sodium perchlorate solution were unharmed after 5 days; two-thirds died after 2 days in 1 per cent solution; and all expired in a 4 per cent solution within 1 hr.[22] Tadpoles were affected after 48 hr in 0.1 per cent sodium perchlorate solution, and in 0.2 per cent solution all died within 36 hr.[22]

The toxicity of sodium perchlorate in rabbits has been investigated extensively by Kahane[40] and by Durand.[22] Autopsies performed on rabbits subjected to repeated injection of sodium perchlorate revealed no evidence of changes in the heart, kidney, or intestines. However, necrosis of the tissue at injection sites, caseation of the liver, and hepatization of the lungs were evident.

According to Selivanova,[11] the minimum lethal dose of ammonium perchlorate is 3.5 g/kg for rats, 2 g/kg for mice and 0.75 g/kg for rabbits.

The general toxic effects of perchloric acid when administered orally or sub-cutaneously to rats, mice, and dogs have been described in detail by Selivanova and coworkers.[41] In addition to its acidic irritating effect, perchloric acid produces a specific antithyroid action and induces abnormalities in hepatic, renal, cardiovascular, and hemapoietic functions when administered internally.

Perchloric acid is reported to cause dermatitis if permitted to act directly on the skin in sufficient amount or concentration for a sufficient length of time.[42,43] Although its corrosive or irritating action is not as immediate nor quite as damaging as concentrated nitric, sulfuric, or hydrochloric acid, due caution should be followed in handling it to avoid contacting it with the eyes and skin. In the event of accidental contact the affected area should be washed immediately with large quantities of water. Prompt medical attention should also be received after any contact with the eye.

The inhalation toxicity in rats and mice of the combustion products of rocket propellants containing various amounts of perchlorate has been investigated by Feinsilver, Mac Namee, McGrath, and Oberst.[44]

Toxicological effects of perchloryl fluoride in rodents and dogs have been studied by Kunkel and coworkers.[45,46] The subject also has been reviewed in detail by Levens.[1]

BACTERIAL AND MICRO-ORGANISM STUDIES

Chemical reduction of perchlorate to chloride ions by several species of heterotrophic bacteria has been demonstrated with the use of chlorine-36 labelled perchlorate by Hackenthal and coworkers.[47] The reduction is strictly dependent upon the presence of bacterial nitrate reductase. Perchlorate reduction by *Staphylococcus epidermidis* in complex media is inhibited by nitrate, and nitrate reduction of resting cells of *Bacillus cereus* is inhibited by perchlorate. These results suggest that nitrate and perchlorate ions may be substrates to the same enzyme, nitrate reductase. The rates of reduction of both anions are equally dependent on pH, incubation temperature, and several electron donor and cofactors.[48] Moreover, both activities are inhibited by cyanide, azide, and 2,4-dinitrophenol, as well as by one another in a competitive manner. Perchlorate is reduced first to chlorate and then to chloride by cell-free extracts obtained from nitrate-adapted cells of *B. cereus.* Hackenthal and Arbabzadeh[49] also found that nitrate reduction in cell-free extracts from *B. cereus* and *Pseudomonas aeruginosa* is competitively inhibited by perchlorate, thiocyanate, selenocyanate, chlorate, rhenate, and azide.

The toxicity of aqueous solutions of sodium perchlorate to *Escherichia coli* and other micro-organisms has been described by Durand.[22] Development of E. *coli* and of *Staphylococcus pyogenes aureus* is prevented by concentrations of about 2.5 to 3.0 and 7.5 to 10 per cent, respectively. For the *mold Sterigmatocystis nigra* development is retarded by a concentration of 1.3 and arrested by a 10 per cent solution of sodium perchlorate.

Sodium perchlorate has been found to affect both the respiration and enzymatic activity of soil micro-organisms.[50] In either incubated soil or pure cultures of soil bacteria, sodium perchlorate inhibited the respiratory activity and decreased the number of ammonifying, nitrifying, and denitrifying bacteria. According to Karki and Kasier,[50] the perchlorate acted in 2 ways: by altering metabolites that are toxic to the cells and by competing with nitrate for the nitrate-reductase A enzyme.

Ammonium perchlorate solutions of concentrations 0.5 to 2 mg/ml are reported to have cytostatic or lethal effects on *Paramecium caudatum*, *Saccharomyces cerevisiae*, and *Candida tropicalis*.[51]

PLANT STUDIES

Numerous investigations have been devoted to characterizing the action of perchlorate on plants, prompted in large measure by findings in 1896 by Sjollema[52] that Chile saltpeter contains potassium perchlorate as a contaminate (in amounts ranging from 0 to 6.79 per cent) which can cause damage to plants. The early studies clearly demonstrated that certain levels of sodium or potassium perchlorate were harmful to plants; however, some doubt arose as to whether or not Chile saltpeter normally contains sufficient perchlorate to be injurious to plants if used in fertilizers.[53,54] Sjollema[55,56] pointed out that the sporadic nature and irreproducible results observed for crop damage attributable to use of Chile saltpeter could be accounted for by the fact that potassium perchlorate is not uniformly distributed in the mineral but occurs in pockets. He also observed that certain suppliers had begun (in about 1892) to recycle the saltpeter mother liquor excessively, which could account for a build-up of perchlorate content and the sudden appearance of damage to crops. In 1914, Maschhaupt[57] reported finding a maximum perchlorate content of 1.5 per cent in crude and about 1 per cent in refined saltpeter; in fertilization experiments these levels inhibited plant growth, confirming the findings of Sjollema. More recently, Tollenaar and Martin[58] found that potassium perchlorate in Chilean nitrate was responsible for stunted soybean plants in Chile. The plants were 50 to 67 per cent reduced in size and bore strongly crumpled leaves with burned tips. Clearly there is a need for careful quality control in processing and selecting of Chilean saltpeter for use in fertilizers.

Considering the possible implications to marine vegetation, a 1958 report[59] that perchlorate had been found at 10 to 1000 ppm concentrations in sea water from various localities attracted considerable attention. Extensive and thorough testing by others[60-64] failed to substantiate the claim that perchlorate is an important constituent of sea water. Greenhalgh and Riley[61] attributed the alleged finding of perchlorate to chloride ion interference in the analytical method.

The major action of moderate concentrations of perchlorates on plants is inhibition of growth. Seed germination is also retarded or terminated. Various studies substantiate these general conclusions, at least with regard to plant species studied thus far. Sjollema[52] observed that rye plants grown in pots containing as little as 50 mg of sodium or potassium perchlorate were stunted and bent and bore yellow leaves. Exposure to perchlorate delayed germination of rye seeds and resulted in abnormal embryos. Growth retardation of rye and oats by perchlorates was reported by Maercker[65] and by Caluwe.[66] Lauffs[67] found small amounts of perchlorate to be beneficial to growth but large amounts to be toxic to wheat plants. Root hairs of wheat plants grown for 8 days in dilute perchlorate solution were deformed.[67] Exposure of young wheat and rye plants to 0.2 to 1.0 per cent potassium perchlorate for only a few hours, however, had little effect on root hairs.[68] Ekdahl[69] confirmed these findings by similar experiments with root hairs of young wheat plants grown in water culture. He also found that the toxicity of various chlorine compounds decreased in the following order: hypochlorite, chlorite> perchlorate> chlorate> chloride. Åberg[70] observed, however, greater toxicity for chlorate than for perchlorate in studying the effects of a number of salts on young wheat plants grown in nutrient solution.

The toxicity of perchlorates vary with the type of plant, culture or soil in which the plant is grown, and lighting conditions to which the plant is exposed. The relative toxicity of perchlorate to chlorate apparently may vary also, or even be reversed, from one set of conditions to another. Weaver[71] found that perchlorate was more toxic to Biloxi soybean plants grown in water culture than to those grown in sand; he found the opposite to be true for chlorate. Åberg[70] observed that root injuries to young wheat plants occurred when they were grown in nutrient solution containing 0.5 mmol/l potassium perchlorate, but only for lightgrown plants. Those grown in darkness under similar conditions withstood damage. Cook found that perchlorate is more toxic than chlorate when sprayed on plants grown in soil,[72] even though in solution culture the lethal dose to the plants is about the same (0.25 per cent) for both anions.[73] Perchlorate and chlorate both caused mottling of leaf foliage in young tomato plants, but with different characteristics, in experiments reported by Owen.[74]

Alvisi and Orabona[75] observed that solutions of potassium perchlorate were initially harmful but eventually beneficial to bean plants. With ammonium perchlorate, the anion appeared to be decomposed by the bean plant, while potassium perchlorate was unchanged. Similarly, *Penicillum glaucum* reduced ammonium perchlorate but not potassium perchlorate. Treatment of a 0.2 per cent potassium perchlorate solution with pepsin, papain, or diastase for 1 to 6 days at room temperature failed to produce detectable chloride ion levels.

Weiske[54] found that germination of grains and vegetables was retarded by exposure of the seeds to potassium perchlorate. Germination of the seeds of *Pisum sativum* was only slightly decreased by soaking 24 hr in 1 per cent potassium perchlorate, according to Vandevelde.[76] In experiments conducted by Durand,[22] seeds of poppy, lentil and flax germinated almost normally in 0.2 per cent sodium perchlorate, but they were affected appreciably in 0.5 per cent solution.

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CHAPTER VIII

SAFETY AND ENVIRONMENTAL CONCERNS

Those who would employ perchloric acid or perchlorate compounds to good advantage in any of the many and valued applications known for these substances should be mindful of the hazards involved. There resides in most perchlorates an awesome oxidation power which, if unleashed in force upon oxidizable matter, can give rise to conflagrations or fierce explosions. Although calamity awaits anyone who would use a source of power carelessly, there are sensible and safe methods available to harness and control power for useful purposes. In the case of perchlorates, the essential guidelines for safeguarding against unleashed power and havoc involve the following measures: (1) control of both temperature and concentration, (2) exclusion of certain substances from contact with perchlorates to prevent reactions that produce unstable perchlorates, and (3) minimization of amounts of oxidizable matter that can come into contact with any perchlorate at any one time. The ferocity of the oxidation power of perchlorates thus can be controlled as needed in any application.

Specific precautions and safety measures in handling and storing perchloric acid and perchlorates are summarized in the following sections. For a clearer understanding of the risks and safety measures, the properties of perchloric acid and of the perchlorates should be reviewed in Chapters II, III, and VII. Other sources[1-4] may also be consulted.

Some Reported Perchlorate Explosions

Reports of early investigators attest to the fact that anhydrous perchloric acid is not only exceedingly corrosive to the skin and mucous membranes but explosively unstable.[5,6] It should not be prepared except for special needs nor stored except at low temperature and then only in small quantities and for short periods.[5-7] The monohydrate, although considerably more stable and storable for long periods in sealed glass ampoules without discloration,[7] can react explosively with organic matter.[5,8]

Explosions have been reported for various perchloric acid mixtures. The most tragic was that which caused the death of 17 persons in Los Angeles, California, on February 20, 1947. It apparently occurred as a result of the introduction of a plastic holder into an electropolishing mixture consisting of approximately 150 gal. of 68-72% perchloric acid and 20 gal. of acetic anhydride, contained in a stainless steel tank (phenolic resin-coated) and fitted with a refrigeration system that had been shut off.[9,10] The unfortunate combination of elevated temperature, concentrated perchloric acid, and reactive organic matter resulted predictably in the inevitable. Other mixtures for which explosions have been reported on subjection to high temperature include those with aqueous perchloric acid and the following: alcohols,[11,12] hydrogen,[13] wood,[14] acetic anhydride (containing more than 57% by volume $HClO_4$),[15] bismuth metal,[16] easily oxidizable organic materials,[17] sodium hypophosphite,[18] sulfoxides,[19] phenol,[19] and various wet-oxidation mixtures which were not adequately preoxidized by treatment with nitric acid[20-22]

It should be emphasized that aqueous perchloric acid solutions of concentration 72% by weight or less are remarkably stable to heat and shock, provided that reactive material is absent. For example, Dietz[13] reported that boiling 72% perchloric acid could not be detonated when primed with mercury fulminate or lead azide. Introduction of an electrical arc into the boiling acid produced only weak, local deflagrations.

Some of the most hazardous perchlorate compounds reported are those that are most sensitive to heat or shock. They include the highly explosive diazonium perchlorates,[23] silver perchlorate,[24,25] hydrazine perchlorate,[26] fluorine perchlorate,[27] and perchlorate esters of aliphatic alochols.[28-31] Other perchlorate compounds for which explosions have been reported on heating or by detonation are the following: aniline perchlorate,[32] pyridine perchlorate,[33] benzyl perchlorate,[34] silver perchlorate-benzene complex,[35] dimethylamine perchlorate,[36] tris(ethylthio)cyclopropenylium perchlorate,[37] and 1,3-dithiolium perchlorate.[38] The perchlorates cited here serve only as examples; they certainly do not constitute a complete list of hazardous perchlorates. It is both reasonable and wise to assume that all organic perchlorate and most heavy metal perchlorates are capable of explosive decomposition under certain conditions. There is no substitute for cautious experimentation guided by diligent attention to lessons from the past.

Precautions in Use and Handling of Perchloric Acid

Various agencies, organizations, and individuals have formulated recommendations concerning the handling, storage, and dispensing of aqueous perchloric acid. These include the Manufacturing Chemists' Association,[39] the National Safety Council,[40] the Factory Mutual Engineering Division,[41] the Association of Casualty and Surety Companies,[42] the Association of Official Agricultural Chemists,[43] the Analytical Methods Committee of the Society of Analysts,[44] Harris,[45] Muse,[3] Gawen,[46] the National Fire Protection Association,[47] and Everett and Graf.[48] Many of these rules and recommendations are summarized below. However, as emphasized by Levens,[2] the prospective user should not rely unquestioning only on rules but rather should "first become familiar with the properties of perchloric acid, and then, for each case, give the most careful consideration to the proposed experimental conditions and operating procedure." Some of the most important properties of perchloric acid in this regard are therefore also cited in the list of precautions that follows:

1. Anhydrous perchloric acid is extremely unstable and will explode spontaneously. Its preparation should be avoided.

2. Aqueous perchloric acid in concentrations less than 85% is completely stable under ordinary storage conditions. The concentrations normally supplied commercially are 60 and 72%

3. Boiling or evaporation of an aqueous solution of perchloric acid will not produce a dangerously high concentration because an azeotropic mixture results which at 760 mm pressure contains 72.5% $HClO_4$ and boils at 203°C. If metallic salts are present, however, the mixture should not be evaporated to dryness over an open flame.

4. The dangerously explosive anhydrous acid may form accidentally if the aqueous acid is subjected to strong dehydrating conditions, such as provided by hot, concentrated sulfuric acid or phosphorus pentoxide. Special care is required

in performing analyses requiring the use of perchloric acid with such agents.

5. Hot and concentrated perchloric acid (60 to 72%) is a powerful oxidant, but it loses its oxidation strength when cooled or diluted with water. Organic and combustible materials are readily oxidizable by hot, concentrated perchloric acid, some explosively. The major source of danger in handling and storage of perchloric acid arises from the risk of contact with oxidizable material accompanied or followed anytime thereafter by exposure to high temperature.

6. Perchloric acid reacts with alcohols and certain other organic compounds to form very unstable (shock or heat) perchlorate esters. Dilute solutions of these may be reasonably safe but extreme caution should be exercised to avoid concentrating them by evaporation or other laboratory procedures.

7. When perchloric acid is used for the destruction of organic matter, preliminary treatment with nitric acid or mixtures of nitric and perchloric acids is recommended. Nitric acid moderates the reaction by oxidizing the more reactive components at lower temperatures, before the perchloric acid becomes sufficiently concentrated to begin its oxidation action. Wet oxidation of heterocyclic nitrogen compounds, fats, oils, and certain other reactive substances that are immiscible in perchloric acid require special treatment (see Chapter IV).

8. *When filter paper is used to collect precipitates from* solutions that contain perchloric acid (even if dilute), the filter paper and precipitate should not be dried before thorough washing with water or suitable aqueous solution to remove all of the perchloric acid. Glass or porcelain filter crucibles should be used in place of filter paper, and no precipitate should be dried unless it is known to be stable at elevated temperatures.

9. Safety equipment should be employed whenever perchloric acid is used in high concentration and/or at elevated temperatures. Safety glasses, cleanliness, pipet bulbs, and other routine safety measures are advisable at all times. A special fume hood or fume eradicator (see below), portable safety shield, and heat-resistant glassware should be em-

ployed for perchloric acid digestions and wet oxidation procedures. A fire extinguisher and safety shower should also be at hand.

10. Perchloric acid spills should be diluted immediately with water, taken up with swabs (preferably wool), and then washed with generous amounts of water. The swabs should also be washed with water before discarding. Swabs of cotton or other cellulose material contaminated with perchloric acid should be regarded as fire or explosion hazards if not washed throughly with large amounts of water.

11. Perchloric acid should be kept apart from organic chemicals and reducing substances, especially alcohol, glycerol, and hypophosphites. Bottles of the acid should stand in glass or porcelain dishes on ceramic or other non-absorbing and non-inflammable benches, shelves, or supports. Flooring and furnishings near the stored acid should be of noncombustible and nonabsorbent materials also.

12. Organic matter (such as paper, wood, grease, plastic, or cloth) which has been exposed to perchloric acid fumes or solutions should be regarded as a fire or explosion hazard until it has been washed thoroughly with water and tested. A small sample (0.01 to 0.10g) placed on a hot-plate will indicate whether or not the material has become unduly inflammable.

Precautions in Handling Perchlorates

No generally applicable set of recommendations have been promulgated for the safe handling of perchlorates. Several sources of information regarding hazards and precautions, however, are available for some. These include articles and reports by Burton and Praill,[1] Levens,[2] Wolsey,[49] Davis,[23] and Elliott and Brown.[17] Safety requirements for perchlorate propellant mixtures have been summarized by Warren[50] together with details of plant layout and design, equipment, operating procedures, storage, and transportation. Another source of information on handling and storage of perchlorate propellant and explosive mixtures is the Ordnance Safety Manual of the U.S. Army Ordnance Corp.[51]

Covalent perchlorate compounds, such as organic perchlorates and certain heavy metal perchlorates, tend to be dangerously explosive. The higher the degree of covalent character, the greater the explosive tendency. Ionic perchlorates, such as the alkali and alkaline earth metal perchlorates and rare earth metal perchlorates, generally have much higher stabilites. Other than these simple qualitative distinctions, no simple guidelines exist for predicting the degree of hazard associated with any given perchlorate. Each must be evaluated separately in the context of its use. Several general precautions, however, are applicable to all:

1. Exposure of the pure compounds to high temperature, mechanical shock, or easily oxidized organic matter greatly increases the risk of fire or explosion.
2. Perchlorate salts that have come into contact with organic solvents should not be heated, subjected to shock, or discarded without first adding a large amount of water.
3. When undertaking to prepare or use any perchlorate for the first time one should review the literature for possible risks and start with very small quantities to become acquainted with its properties and any hazards involved.
4. Anhydrous magnesium and barium perchlorates should not be used as desiccants or dehydrating agents for samples that contain volatile organic matter, such as ether or alcohol. Spent desiccant should not be regenerated by drying until first recrystallizing it from water to counteract any possibility that organic vapors have been absorbed.
5. Aqueous perchlorate solutions that contain heavy metal ions or organic matter should not be evaporated to dryness by heating. Extreme caution should be exercised in scraping or agitating unknown solid products obtained from perchlorate solutions.

Perchloric Acid Fume Hood and Eradicators

Digestions and other routine operations involving production of perchloric acid fumes should be carried out in specially designed hoods reserved solely for that purpose. If a suitable hood is not available, special apparatus or a glass fume-eradicator should be employed. No organic materials should be stored in the hood. An oil bath should never be used for heating. Electric heating mantles and hot plates of the vapor proof type to protect against corrosion from acid fumes should be used instead of open flames. The floor and furnishings surrounding the hood or fume-eradicator should be clean, non-absorbent, and constructed of inorganic material.

The construction of fume hoods for perchloric acid service has been described by various workers.[52-56] A stainless steel fume hood was described by Dieter and coworkers,[54] and a polyvinyl chloride system was designed by Boies.[55] Most incoporate the following recommendations, set forth by the Factory Mutual Engineering Division:[41]

> Fume hoods should be noncombustible, contructed of metal or stoneware, and left unpainted or protected with an inorganic coating such as porcelain. A water spray is desirable for washing down the hood after perchloric acid fuming. Otherwise, a separate hood should be reserved for perchloric acid use only. Stoneware hoods equipped with water spray for washing down are commercially available. Ducts must not be manifolded and should take the shortest path to outdoors. Use an electric hot plate or heating jacket, a steam bath, or an electrically or steam-heated sand bath for heating reaction vessels. Do not use gas flames or oil bath for heating. Provide a generous supply of water-type fire extinguishers.

Some special recommendations that should be considered in the design and construction of fume hoods for perchloric acid are the following:

1. Grouting material and cements for sealing the hood should not contain organic constituents. For example, litharge and glycerine cement should not be used. Pastes of Alundum cement and sodium silicate or similar materials are satisfactory.[44]

2. Bends, horizontal runs, and porous construction materials should be avoided in constructing the exhaust system. A vertical exhaust system which will not collect dust or distillate is preferred.[3]

3. A washdown system should be incorporated in the ductwork (as well as the hood proper) to wash out all deposits daily.[3]

Recommendations as to how to dismantle perchlorates contaminated lab exhaust systems have been given by

Breysse and Lehman,[57] together with recommendations for the installation of safe systems. Wolsey[58] has described a *simple test* for perchlorates and perchloric acid in hoods and chemical apparatus, based upon the reaction with methylene blue to give a violet precipitate with perchlorate ion.

A portable, self-contained laboratory scrubber unit was described by Silverman and First.[59] Designed to be placed in a standard lab hood, the unit incorporates a wet absorption stage, a droplet eliminator, and a dry filter. It was reported that up to 99.9% of the perchloric acid fumes from acid digestions could be eliminated through use of the unit.

Smith designed a perchloric acid fume eradicator for convenient use in the open laboratory.[60,61] The apparatus is illustrated in Figure 4.1 and is commercially available from the G. Frederick Smith Chemical Company. It includes a refluxing still head to prevent loss of spray from the hot acid, a glass fume collector that surmounts and envelops the top of the reaction flask and refluxing still head, and an aspirator flask attached to the fume collector and filled with sodium hydroxide solution to scrub the aspirated fumes which pass thru it and out into the water aspirator. The fume eradicator may be placed in position with ease and readily removed and set aside, being supported by the weight of the aspirator flask and its contents.

A modified distillation unit for performing perchloric acid digestions without a special fume hood was described by Griffen and Hocking.[62] It is constructed from a regular long-necked borosilicate glass Kjeldahl flask and fitted at the top with a distilling head connected by a large polished glass, spherical joint separated by a perchloric acid resistant Telflon-covered silicone rubber o-ring. The condenser is fed into a double-sphere anti-suckback drip tube which discharges into 350-400 ml of cold water.

Environmental Pollution

Disposal of waste perchlorates and perchloric acid in small quantities, such as expended in ordinary laboratory procedures, is commonly accomplished by flushing the wastes into sewer drains with generous quantities of water. This expediency is much safer than accumulating the wastes for special treatment and separate disposal. No adverse effects to plants or animals from small concentrations (up to 100 ppm as $KClO_4$) of perchlorate have been reported. Biological effects of perchlorates are summarized in Chapter VII.

To the writer's knowledge, no problem has been encountered in sewage treatment plants arising from the disposal of perchlorate wastes from ordinary laboratory operations. The disposal of large quantities of waste perchlorates, however, is a different problem because concentrations of perchlorate at the 0.1 to 1.0% and above levels are known to affect certain aquatic life and soil micro-organisms. Here, the safest and most expedient approach appears to be biodegradation of the waste perchlorates before discharging into streams or landfills.

A method for purification of industrial waste waters from perchlorates and chlorates has been described in patents by Koren'kov, Romanenko, Kuznetsov, and Voronov.[63-65] The perchlorates and chlorates are reduced anaerobically by a micro-organism classified as *Vibrio dechloraticans*, isolated from a mixture of industrial and domestic sewage containing perchlorates.[66] An example described in the patents follows. Industrial waste water containing 600 mg NH_4ClO_4/l and clarified domestic sewage (BOD 180 mg/l) were pumped into a bioreducer at rates such that the ammonium perchlorate concentration and the biological oxygen demand of the mixture was 100 mg/l and 150 mg/l, respectively. An enriched culture of *V. dechloraticans (Cuznesove B-1168)* was continuously pumped into the bioreducer so that its concentration was 3.5 g/l based on the biomass solids. During the one-hour residence time of the culture and mixture in the bioreducer the perchlorate was completely reduced to chloride. The rate of reduction of perchlorate was 28 mg/g biomass solids-hour.

The rate of biodegradation and its effect on the environment has been studied in terms of growth, metabolic rate, and total biomass of selected animal and plant species.[67] Short term effects on selected organisms were investigated, and a long term experiment was designed to assess the changes incurred by ammonium perchlorate on nitrogen and chloride contents of soil over a three-year period.[68]

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APPENDIX

PHYSICAL AND EQUILIBRIUM DATA FOR BINARY, TERNARY, AND QUATERNARY SYSTEMS OF PERCHLORATES

The sheer quantity of physical data available for the many different mixed perchlorate systems precludes detailed presentation in a monograph of this kind. Therefore, in place of the data, a reasonably complete bibliography of the published literature on the subject is presented in systematic fashion in the tables which follow.

References are cited by number in the tables and identified in the list of references at the end of this Appendix. For brevity, several of the more commonly cited journals are abbreviated as follows:

Abbreviation	*Name of Journal*
UZY	Uch. Zap., Yaroslav. Gos. Pedagog. Inst.
SNT	Sb. Nauch. Tr. Yaroslov. Gas. Ped. In-t
ZNK	Zh. Neorg. Khim.

TABLE 14

BIBLIOGRAPHY ON PERCHLORATE CONDUCTIVITIES

Solute	*Solvent*	*References*
$HClO_4$	Dioxane-water mixtures at 18°	1
$HClO_4$ + NaOAc	Acetic acid-water mixtures	2
$LiClO_4$	n-Propyl alcohol	3
$LiClO_4$	Tetrahydrofuran, propylene carbonate, and mixtures	4
$LiClO_4$	Aliphatic alcohols	5
$LiClO_4$	Dimethyl sulfoxide-sulfolane mixtures	6
$NaClO_4$	Dimethyl sulfoxide-sulfolane mixtures	6
$NaClO_4$	Tetrahydrofuran	7
$NaClO^4$	Water-glycine mixtures	8
$NaClO_4$	Acetone-dioxane mixtures	9
Alkali metal perchlorates	Ethylene glycol	10
Alkali metal perchlorates	Hexamethylphosphoramide	11
Alkaline earth perchlorates	Hexamethylphosphoramide	11
Tetralkylammonium perchlorates	Hexamethylphosphoramide	11
Rare earth perchlorates	Water	12

TABLE 15

BIBLIOGRAPHY ON PHYSICAL PROPERTIES OF MOLTEN BINARY MIXTURES

Mixture	*Properties*	References
$LiClO_4$-$NaClO_4$	Conductance	13, 16
$LiClO_4$-$KClO_4$	Conductance	14, 16
$MClO_4$-MNO_3(M=alkali metal)	Conductance	15
$LiClO_4$-$NaClO_4$	Viscosity	17
$LiClO_4$-$KClO_4$	Viscosity	17
$MClO_4$-MNO_3(M=Li,Na, or K)	Viscosity	18
$Ca(ClO_4)_2$-$KClO_4$	Thermal	19
$Ba(ClO_4)_2$-$KClO_4$	Thermal	19
$Ca(ClO_4)_2$-$Ba(ClO_4)_2$	Thermal	19
$LiClO_4$-$NaClO_4$	Density and molar volume	20
$LiClO_4$-$KClO_4$	Density and molar volume	20
$LiClO_4$-$NaClO_4$-$KClO_4$	Melting behavior	21

TABLE 16

BIBLIOGRAPHY ON TERNARY SYSTEMS

(Water-M_1Perchlorate-M_2Perchlorate)

M_1	M_2	*Measurements*	*References*
H	Li or Na	Osmotic pressure and activity coefficients	22
H	Na	Solubility, viscosity, P_{H_2O} at 25°	23
H	Rb or Cs	Solubility at 25°	24
H	Ca or Cd	Solubility at 25°	25
H	Ca	P_{H_2O} at 25°	26
H	Mg,Ca Sr, or Ba	Solubility at 0°, 25°, and 50°	27
H	Be	Solubility at 25°	28
H	Be,Cd or Hg	P_{H_2O} at 25°	29
H	Hg	Solubility at 0°, 25°, and 50°	30
H	Mn, Co, or Ni	Solubility at 25°	31
H	Cu or Zn	Solubility at 25°	32
H	Cu	P_{H_2O} at 25°	33
H	Sc or Nd	Solubility at 25°	34
H	Ce	Solubility at 0° and 20°	35
NH_4	Li	Solubility, density, viscosity, conductance at 25°	36
NH_4	Na	Solubility at 25°, 35°, and 90°	37, 38
NH_4	Mg	Solubility at 25° and 50°	39, 40, 41

TABLE 16—(Continued)

M_1	M_2	*Measurements*	References
NH_4	Mg	Density and viscosity of saturated solutions at 40°	42
NH_4	Ca	Solubility, density, viscosity, conductance at 40°	43
NH_4	Sr	Solubility, density, viscosity, refractive index at 25°	44, 45, 46
NH_4	Rb	Solubility, density, viscosity, at 25°	47
NH_4	Ba	Solubility, density, viscosity, at 25°	48
NH_4	Co	Solubility at 25°	49
NH_4	Ni	Solubility, density, viscosity at 25°	50
NH_4	Cu	Solubility at 25°	51
NH_4	Zn	Solubility at 25°	52
NH_4	In	Solubility at 25°	53
NH_4	Tl	Solubility, conductance at 25°	54
NH_4	Ce	Solubility at 25°	55
Li	Na	Solubility, density, viscosity, refractive index at 25°	56
Li	Na	Solubility at 50°	57
Li	K	Solubility, density, viscosity at 25°	58
Li	Mg	Solubility, density, viscosity, conductance at 25°	59
Li	Ca	Solubility at 25°	60
Li	Ba	Solubility at 25°	61
Li	Co	Solubility at 25°	62

Li	Ni	Solubility at 25°	62
Li	Cu	Solubility at 25°	63
Li	Tl	Solubility at 25°	64
Li	Tb	Solubility at 25°	65
Na	K	Solubility at 25°	66
Na	Cs	Solubility at 25° and 75°	67
Na	Ca	Solubility, density, viscosity, refractive index at 40°	68
Na	Sr	Solubility at 25°	69
Na	Ba	Solubility, density, viscosity at 25° and 50°	70
Na	Ni	Solubility, density, viscosity at 25°	71
Na	Zn	Solubility at 25°	72
Na	Tl	Solubility at 25°	73
Na	Ce	Solubility at 25°	74, 75
Na	Tb	Solubility at 25°	76
K	NH_4	Vapor pressure at 25°	77
K	Rb or Cs	Solubility at 25°	78, 79
K	Mg	Solubility, density, viscosity, refractive index at 25°	80
Mg	Ca	Solubility, density, viscosity, conductance at 25°	81
Mg	Ni	Solubility at 25°	82
Mg	Tl	Solubility at 25°	83
Mg	La	Solubility at 25°	84
Ca	Zn	Density at 25°	85

TABLE 16—*(Continued)*

M_1	M_2	*Measurements*	*References*
Ca	Mg or Ce	Solubility at 25°	86
Sr	Pr	Solubility at 25°	87
Ba	Pr	Solubility at 25°	87
Ba	Ce	Solubility at 25	88
Mn	Co or Ni	Solubility at 25°	89
Mn	Ni	Solubility at 50°	90
Mn	Tl	Solubility at 25°	91
Mn	Ce	Solubility at 25°	92
Co	Cd	Solubility at 25°	93
Co	Ni	Solubility at 25°	94
Co	Tl	Solubility at 25°	95
Co	Pr	Solubility, density, viscosity, conductance at 25°	96, 97
Co	Nd	Solubility at 25°	98
Ni	Tl	Solubility at 25°	99
Ni	La	Solubility at 25°	100
Cu	Tl	Solubility at 25°	101
Cd	Pr	Solubility, density, viscosity, conductance at 25°	96, 102
Tl	Ca	Solubility at 25°	103
Tl	La	Solubility at 25°	104

TABLE 17

BIBLIOGRAPHY ON TERNARY SYSTEMS

(Water-Perchlorate-Other Solute)

Perchlorate	*Other Solute*	*Measurements*	*References*
H	H_2SO_4	Phase diagrams	105
H	Urea or Thiourea	Solubility at 0°, 20° and 40°	106
Li	$LiNO_3$	Solubility at 50°	107
Li	Li_2CrO_4	Solubility, density, viscosity and conductance at 25°	108
Li	Acetamide	Solubility at 25°	109
Li	Hexamethylenetetramine	Solubility at 25°	110
Li	NaCl	Solubility, density at 0°-100°	111
Na	NaCl or $NaClO_3$	Solubility, density, viscosity, conductance at 60°	112
Na	$NaNO_3$	Solubility at 25° and 50°	113
Na	Na_2SO_4	Solubility at 25° and 60°	114
Na	$NaBH_4$	Solubility at 0°	115
Na	Acetamide	Solubility at 25°	116
Na	Hexamethylenetetramine	Solubility, density, viscosity, conductance at 25°	117
Na	Thiourea	Solubility, density, viscosity, conductance at 25°	118
Na	Urea	Solubility at 25°	119
K	KCl	Solubility at 150°-250°	120
K	NaCl	Solubility, density at 0°-100°	121

TABLE 17—(*Continued*)

Perchlorate	*Other Solute*	*Measurements*	*References*
K, Rb, Cs	Acetamide	Solubility at 25°	122
Cs	CsCl	Solubility at 25° and 75°	123
NH_4	NH_4OH	Solubility at 25°	124
NH_4	$(NH_4)_2Cr_2O_7$	Solubility, density, viscosity, refractive index at 25°	125
NH_4	$(NH_4)_2SO_4$	Solubility at 25° and 60°	114
NH_4	NaCl	Solubility at 25°, 50° and 80°	126
NH_4	Acetamide	Solubility at 25°	127
Mg	Acetamide	Solubility at 25°	128
Mg	Hexamethylenetetramine	Solubility at 25°	129
Ca	$Ca(NO_3)_2$	Solubility at 25°	130, 131
Ca	Hexamethylenetetramine	Solubility at 25°	132
Ca	Urea	Solubility at 25°	133
Sr	$Sr(NO_3)_2$	Solubility at 25°	134
Sr	Urea	Solubility at 25°	135
Ba	$Ba(NO_3)_2$	Solubility, density, viscosity at 25°	136
Ba	Hexamethylenetetramine	Solubility at 25°	137
Ba	Thiourea	Solubility at 30°	138
Ba	Urea	Solubility at 25° and 30°	138, 139
Mn	$MnSO_4$	Solubility at 25°	140

Mn	Thiourea	Solubility at 25°	141
Mn	Urea	Solubility at 25°	142
Co	$CoCl_2$	Solubility at 25°	143
Co	Acetamide	Solubility at 25°	144
Co	Urea	Solubility at 25°	145
Ni	$NiCl_2$	Solubility, density, viscosity at 25°	146
Ni	$Ni(NO_3)_2$	Solubility, density, viscosity, conductance at 25°	147
Ni	$NiSO_4$	Solubility, density, viscosity at 25°	148
Cu	$CuSO_4$	Solubility at 25°	149
Zn	$ZnSO_4$	Solubility at 25°	150
Cd	$CdSO_4$	Solubility at 25°	151
Cd	Thiourea	Complex formation at 25°	152
Cd, Zn	Urea	Solubility at 25°	153, 154
Tl	$TlNO_3$	Solubility at 25°	155
Tl	Tl_2SO_4	Solubility at 25°	156
Tl	Urea	Solubility at 25°	157
Pr	Thiourea	Solubility at 25°	158
Sm	Thiourea	Solubility at 25°	159
Gd	Thiourea	Solubility at 25°	160
Tb	Thiourea	Solubility at 25°	161
Ho	Thiourea	Solubility at 25°	162
Er	Thiourea	Solubility at 25°	163

TABLE 18

BIBLIOGRAPHY ON QUATERNARY AQUEOUS SYSTEMS

Perchlorates of	*Other Solute*	*Data Reported*	*References*
H, Li, and Na	....	Osmotic coefficients at 25°	164
H and V	Vanadic acid	Identity of solid phases	165
NH_4 and Na	NH_4Cl or NaCl	Solubilities at 90°	166
NH_4 and Sr	NH_4NO_3 or $Sr(NO_3)_2$	Solubilities at 25°	167
NH_4 and Ba	NH_4NO_3 or $Ba(NO_3)_2$	Solubilities at 25°	168
Li and Cd	LiCl	Ultrasound compressibilities	169
Na and Ni	Urea	Solubilities at 25°	170
Na and Ni	$NaNO_3$ or $Ni(NO_3)_2$	Solubilities at 25°	171
Mg and Ce	$MgCl_2$ or $CeCl_3$	Solubilities at 25°	172
Mg and Ca	Thiourea	Solubilities at 25°	173
Co and Ni	Thiourea	Solubilities at 25°	174
Co and Ni	Urea	Solubilities at 25°	175
Co and Pr	Thiourea	Solubilities at 25	176
Co and Pr	Urea	Solubilities at 25°	177

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