

Kirk-Othmer

Encyclopedia of
Chemical Technology

Second Edition

VOLUME 5

Kirk-Othmer

ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY

Second completely revised edition

VOLUME 5

Chlorine
to
Colors for Foods,
Drugs, and Cosmetics

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ABBREVIATIONS AND SYMBOLS

A	ampere(s)	aq	aqueous
<i>A</i>	anion (eg, HA)	<i>ar</i> -	aromatic (eg, <i>ar</i> -vinyl-aniline)
Å	angstrom unit(s)	Ar	aryl
AATCC	American Association of Textile Chemists and Colorists	<i>as</i> -	asymmetric(al) (eg, <i>as</i> -trichlorobenzene)
abs	absolute	ASA	American Standards Association
ac	alternating current	ASHRAE	American Society of Heating, Refrigeration and Air-Conditioning Engineers
<i>ac</i> -	alicyclic (eg, <i>ac</i> -derivatives of tetrahydronaphthalene)	ASM	American Society for Metals
accel(d)	accelerate(d)	ASME	American Society of Mechanical Engineers
acceln	acceleration	ASTM	American Society for Testing and Materials
ACS	American Chemical Society	atm	atmosphere(s), atmospheric
addn	addition	at. no.	atomic number
AGA	American Gas Association	at. wt	atomic weight
Ah	ampere-hour(s)	av	average
AIChE	American Institute of Chemical Engineers	b	barn(s)
AIME	American Institute of Mining and Metallurgical Engineers	b (as in b_{11})	boiling (at 11 mm Hg)
AIP	American Institute of Physics	bbl	barrel(s)
alc	alcohol(ic)	BC	body-centered
alk	alkaline (not alkali)	Bé	Baumé
Alk	alkyl	Bhn	Brinell hardness number
A-min	ampere-minute(s)	bp	boiling point
amt	amount (noun)	BP	<i>British Pharmacopoeia</i> (General Medical Council in London)
anhyd	anhydrous	Btu	British thermal unit(s)
API	American Petroleum Institute		
app	apparatus		
approx	approximate(ly)		

bu	bushel(s)	cu	cubic
C	centigrade; coulomb(s)	d	density (conveniently, specific gravity)
C-	denoting attachment to carbon (eg, <i>C</i> -acetyl- indoline)	<i>d</i>	differential operator
ca	circa, approximately	<i>d</i> -	<i>dextro</i> -, dextrorotatory
cal	calorie(s)	D	Debye unit(s)
calcd	calculated	D-	denoting configurational relationship (as to <i>dextro</i> -glyceraldehyde)
cfm, ft ³ /min	cubic foot (feet) per minute	db	dry-bulb
cg	centigram(s)	dB	decibel(s)
cgs	centimeter-gram-second	dc	direct current
Ci	curie(s)	dec,	
CI	Colour Index (number); the CI numbers given in <i>ECT</i> , 2nd ed., are from the new <i>Colour Index</i> (1956) and Suppl. (1963), <i>Soc. Dyers Colourists</i> , Bradford, England, and <i>AATCC</i> , U.S.A.	decomp	decompose(s)
cif	cost, insurance, freight	decompd	decomposed
cl	car lots	decompn	decomposition
cm	centimeter(s)	den	denier
coeff	coefficient	den/fil	denier per filament
compd,		deriv	derivative
cpd	compound (noun)	detd	determined
compn	composition	detn	determination
concd	concentrated	diam	diameter
concn	concentration	dielec	dielectric (adj.)
cond	conductivity	dil	dilute
const	constant	DIN	Deutsche Industrienormen
cont	continued	distd	distilled
cor	corrected	distn	distillation
cp	chemically pure	dl	deciliter
cP	centipoise(s)	<i>dl</i> -, <i>DL</i>	racemic
cpd,		dm	decimeter
compd	compound (noun)	dp	dewpoint
cps	cycles per second	dyn	dyne(s)
crit	critical	<i>e</i>	electron
cryst	crystalline	ed.	edited, edition, editor
crystd	crystallized	elec	electric(al)
crystn	crystallization	emf	electromotive force
cSt	centistokes	emu	electromagnetic unit(s)
		en	entropy unit(s)
		eng	engineering
		equil	equilibrium(s)
		equiv	equivalent
		esp	especially
		est(d)	estimate(d)
		estn	estimation
		esu	electrostatic unit(s)

eV	electron volt(s)	ibp	initial boiling point
expt(l)	experiment(al)	ICC	Interstate Commerce Commission
ext(d)	extract(ed)	ICT	International Critical Tables
extn	extraction	ID	inner diameter
F	Fahrenheit; farad(s)	in.	inch(es)
<i>F</i>	faraday constant	insol, i	insoluble
FC	face-centered	IPT	Institute of Petroleum Technologists
Fed, fedl	federal (eg, Fed Spec)	ISO	International Organization for Standardization
fl oz	fluid ounce(s)	IU	International Unit(s)
fob	free on board	IUPAC	International Union of Pure and Applied Chemistry
fp	freezing point	J	joule(s)
frz	freezing	K	Kelvin
ft	foot (feet)	<i>K</i>	dissociation constant
ft ³ /min, cfm	cubic foot (feet) per minute	kbar	kilobar(s)
ft-lb	foot-pound(s)	kc	kilocycle(s)
g	gram(s)	kcal	kilogram-calorie(s)
<i>g</i>	gravitational acceleration	keV	kilo electron volt(s)
G	gauss	kg	kilogram(s)
<i>G</i>	Gibbs free energy	kG	kilogauss
gal	gallon(s)	kJ	kilojoule(s)
gal/min, gpm	gallon(s) per minute	kV	kilovolt(s)
g/den	gram(s) per denier	kVA	kilovolt-ampere(s)
<i>gem-</i>	geminal (attached to the same atom)	kW	kilowatt(s)
g-mol	gram-molecular (as in g-mol wt)	kWh	kilowatt-hour(s)
g-mole	gram-mole	l	liter(s)
G-Oe	gauss-oersted(s)	<i>l-</i>	<i>levo-</i> , levorotatory
gpm, gal/min	gallon(s) per minute	<i>L-</i>	denoting configurational relationship (as to <i>levo</i> -glyceraldehyde)
h, hr	hour(s)	lb	pound(s)
hl	hectoliter	LC ₅₀	concentration lethal to 50% of the animals tested
hp	horsepower	lcl	less than car lots
hr, h	hour(s)	LD ₅₀	dose lethal to 50% of the animals tested
hyd	hydrated, hydrous	liq	liquid
hyg	hygroscopic	lm	lumen
i, insol	insoluble		
<i>i</i> (eg, Pr ⁱ)	iso (eg, isopropyl)		
<i>i-</i>	inactive (eg, <i>i</i> -methionine)		
IACS	International Annealed Copper Standard		

ln	logarithm (natural)	n (as, n_D^{20})	index of refraction (for 20°C and sodium light)
log	logarithm (common)	n , ⁿ	normal (eg, <i>n</i> -butyl; Bu ⁿ)
m	meter(s)	<i>N</i>	normal (as applied to concentration)
<i>m</i> -	meta (eg, <i>m</i> -xylene)	<i>N</i> -	denoting attachment to nitrogen (eg, <i>N</i> -methylaniline)
M	metal	neg	negative (adj.)
<i>M</i>	molar (as applied to concentration; not molal)	NF	<i>National Formulary</i> (American Pharmaceutical Association)
mA	milliampere(s)	NMR	nuclear magnetic resonance
mAh	milliampere-hour(s)	NND	<i>New and Nonofficial Drugs</i> (American Medical Association)
manuf	manufacture	no.	number
manufd,		NOIBN	not otherwise indexed by name (ICC specification for shipping containers)
mfd	manufactured	<i>o</i> -	ortho (eg, <i>o</i> -xylene)
manufg,		<i>O</i> -	denoting attachment to oxygen (eg, <i>O</i> -acetylhydroxylamine)
mfg	manufacturing	Ω	ohm(s)
max	maximum	Ω-cm	ohm-centimeter(s)
Mc	megacycle	OD	outer diameter
MCA	Manufacturing Chemists' Association	Oe	oersted(s)
mcal	millicalore(s)	owf	on weight of fiber
mech	mechanical	oz	ounce(s)
meq	milliequivalent(s)	<i>p</i> -	para (eg, <i>p</i> -xylene)
MeV	million electron volt(s)	P	poise(s)
mfd,		pdr	powder
manufd	manufactured	PhI	<i>Pharmacopoeia Internationalis</i> , 2 vols. and Suppl., World Health Organization, Geneva, 1951, 1955, and 1959
mfg,		phr	parts per hundred of rubber or resin
manufg	manufacturing	pos	positive (adj.)
mg	milligram(s)	powd	powdered
min	minimum; minute(s)		
misc	miscellaneous		
mixt	mixture		
ml	milliliter(s)		
MLD	minimum lethal dose		
mm	millimeter(s)		
mM	millimole(s)		
mo(s)	month(s)		
mol	molecule, molecular		
mol wt	molecular weight		
mp	melting point		
mph	miles per hour		
MR	molar refraction		
mV	millivolt(s)		
mμ	millimicron(s)		
ⁿ (eg, Bu ⁿ),			
<i>n</i> -	normal (eg, normal butyl)		

ppm	parts per million	RT	room temperature
ppt(d)	precipitate(d)	s, sol	soluble
pptn	precipitation	^a (eg, Bu ^a), sec-	secondary (eg, secondary butyl)
Pr. (no.)	Foreign prototype (number); dyestuff designation used in <i>AATCC Year Books</i> for dyes not listed in the old <i>Colour Index</i> (1924 ed.; 1928 Suppl.); obsolete since new <i>Colour Index</i> was published (1956 ed.; 1963 Suppl.)	s-, sym-	symmetrical (eg, s-dichloroethylene)
prepd	prepared	S-	denoting attachment to sulfur (eg, S-methylcysteine)
prepn	preparation	SAE	Society of Automotive Engineers
psi	pound(s) per square inch	satd	saturated
psia	pound(s) per square inch absolute	satn	saturation
psig	pound(s) per square inch gage	SCF	standard cubic foot (feet) (760 mm Hg, 60°F)
pt	point	Sch	Schultz number (designation for dyes from <i>Farbstofftabellen</i> , 4 vols., Akademie Verlag, Leipzig, 1931-1939)
pts	parts	sec	second(s)
qual	qualitative	sec-, ^a	secondary (eg, sec-butyl; Bu ^a)
quant	quantitative	SFs	Saybolt Furol second(s)
qv	which see (quod vide)	sl s,	
r	roentgen	sl sol	slightly soluble
R	univalent hydrocarbon radical (or hydrogen); Rankine	sol, s	soluble
rep	roentgen(s) equivalent physical	soln	solution
resp	respectively	soly	solubility
rh	relative humidity	sp	specific
RI	Ring Index (number); from <i>The Ring Index</i> , Reinhold Publishing Corp., N.Y., 1940	sp, spp	species (sing. and pl.)
rms	root mean square	spec	specification
rpm	revolutions per minute	sp gr	specific gravity
rps	revolutions per second	sq	square
RRI	Revised Ring Index (number); from <i>The Ring Index</i> , 2nd ed., American Chemical Society, Washington, D.C., 1960	St	stokes
		STP	standard temperature and pressure (760 mm Hg, 0°C)
		subl	sublime(s), subliming
		SUs	Saybolt Universal second(s)
		sym, s-	symmetrical (eg, sym-dichloroethylene)
		t, temp	temperature

^t (eg, Bu ^t), t-, tert-	tertiary (eg, tertiary butyl)	v-, vic-	vicinal (attached to adjacent atoms)
t-, tert-, ^t	tertiary (eg, t-butyl)	var	variety
TAPPI	Technical Association of the Pulp and Paper Industry	vic-, v-	vicinal (attached to adjacent atoms)
tech	technical	vol	volume(s) (not volatile)
temp, t	temperature	v s, v sol	very soluble
tert-, t-, ^t	tertiary (eg, tert-butyl)	vs	versus
theoret	theoretical	W	watt(s)
Twad	Twaddell	Wh	watt-hour(s)
USP	(The) United States Pharmacopeia (Mack Publishing Co., Easton, Pa.)	wt	weight
uv	ultraviolet	xu (ca 10 ⁻¹¹ cm)	x unit(s)
V	volt(s)	yd	yard(s)
		yr	year(s)

Quantities

Some standard abbreviations (prefixes) for very small and very large quantities are as follows:

deci (10 ⁻¹)	d	deka (10 ¹)	dk
centi (10 ⁻²)	c	hecto (10 ²)	h
milli (10 ⁻³)	m	kilo (10 ³)	k
micro (10 ⁻⁶)	μ	mega (10 ⁶)	M
nano (10 ⁻⁹)	n	giga (10 ⁹)	G (or B)
pico (10 ⁻¹²)	p	tera (10 ¹²)	T
femto (10 ⁻¹⁵)	f		
atto (10 ⁻¹⁸)	a		

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C continued

CHLORINE

The manufacture of chlorine is discussed under Alkali and chlorine industries, Vol. 1, pp. 668-707. Binary chlorides are usually discussed in the article dealing with compounds of the other element; thus, for aluminum chloride see Aluminum compounds; for hydrogen chloride see Hydrochloric acid. See also Chlorine oxygen acids; Chlorocarbons and chlorohydrocarbons.

Chlorine consumption during the 1950s showed a several-fold increase in demand for the production of chlorinated hydrocarbons which are used in the manufacture of insecticides, refrigerants, propellants, silicones, lubricant additives, etc. As specific examples of this increased demand, chloroform production in 1950 utilized approximately 40 tons per day while in 1960 this demand had increased to approximately 190 tons of chlorine per day. During the same years the production of methyl chloride caused an increase in the daily demand for chlorine from 60 to 175 tons. Since the demand for caustic soda did not keep pace with the increase in chlorine demand, and since large quantities of by-product hydrogen chloride are produced in these chlorination reactions, it has been necessary to reprocess considerable amounts of the by-product hydrogen chloride to regenerate chlorine for further reaction demands.

Considerable research and development efforts have centered on various means of oxidizing this by-product hydrogen chloride. The major efforts have centered around four major processes as follows: (a) improvements in the well-known Deacon process of catalytic oxidation using air or oxygen as the oxidizing agent, (b) chlorine liberation processes by action of oxygen on metallic chlorides such as ferric chloride, (c) utilization of the Deacon process with simultaneous chlorination of organics, and (d) reaction to form chlorosulfonic acid (SO_3HCl) followed by catalytic decomposition yielding sulfur dioxide, chlorine, and sulfuric acid (see Hydrochloric acid).

Chlorine, Cl, atomic number 17, is a nonmetallic element, which, at room temperature, exists as a greenish-yellow diatomic gas, Cl_2 , with a characteristic choking odor. The name is derived from the Greek *chloros* meaning pale green or greenish-yellow.

There are two stable isotopes of chlorine, of atomic mass 35 and 37. These occur to the extent of approximately 75.4 and 24.6%, respectively, in the chlorine-containing compounds. Thus the average atomic weight of this element is 35.457. In addition

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there are five radioactive isotopes of atomic mass 33, 34, 36, 38, and 39. The half life of these range from approximately 2.8 seconds for the isotope of atomic mass 33 to 4.4×10^5 years for the isotope of atomic mass 36.

Chlorine is a member of the halogen family of elements (Group VII of the periodic table) and is located vertically between fluorine and bromine, and horizontally between sulfur and the inert gas argon. The electronic configuration of chlorine is $1s^2 2s^2 2p^6 3s^2 3p^5$ electrons. In its binary compounds of hydrogen and the metals, chlorine exhibits an oxidation number of -1 .

For physical properties see Vol. 1, p. 671.

Reactions

Chlorine reacts with hydrogen slowly in the dark, but with explosive violence in sunlight or above 250°C , forming hydrogen chloride. It will combine directly with all metals under suitable conditions which may include the presence of moisture. Dry chlorine, however, may be shipped in steel cylinders, tank trucks, barges, or tank cars. Metallic chlorides, in general, are soluble in water; the exceptions include silver, mercurous, thallous, cuprous, plumbous, and platinous chlorides as well as antimony and bismuth oxychlorides, which are sparingly soluble. Certain of these sparingly soluble chlorides are soluble in an aqueous solution of hydrogen chloride forming complex chlorometallic anions. For example, cuprous chloride is soluble in hydrochloric acid forming HCuCl_2 . Upon dilution, white cuprous chloride is reprecipitated.

Chlorine reacts directly with sulfur, forming sulfur monochloride, S_2Cl_2 , dichloride, SCl_2 , and tetrachloride, SCl_4 ; it reacts with phosphorus, yielding the trichloride, PCl_3 , or the pentachloride, PCl_5 . It combines with iodine, forming the monochloride, ICl , and trichloride, ICl_3 . Compounds of chlorine with fluorine (ClF_3 , ClF) and with bromine (BrCl) have been described in the chemical literature. Chlorine does not react directly with nitrogen, but excess chlorine or hypochlorous acid will react with ammonium salts in acidic solution, producing nitrogen trichloride, NCl_3 , an oily liquid which is highly explosive,



In dilute, equimolar solutions of ammonia and hypochlorite, the unstable chloramine (chloramide), NH_2Cl , is formed,



Treatment of chloramine with additional ammonia results in the formation of hydrazine (qv), N_2H_4 , an important reducing agent which is used as a fuel in certain U.S. rocket propellants (qv),



The general preparation of hydrazine entails reacting chlorine with excess ammonia,



Dichloramine, NHCl_2 , is formed similarly.

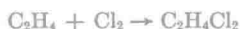
Chlorine will react with many hydrocarbons, replacing one or more hydrogen atoms and forming hydrogen chloride as a by-product. Thus with methane the initial product is methyl chloride,



By successive substitutions dichloromethane, CH_2Cl_2 , chloroform, CHCl_3 , and carbon tetrachloride, CCl_4 , are formed. With other hydrocarbons, such as turpentine, chlorine decomposes the molecule into hydrogen chloride and carbon.



With unsaturated hydrocarbons, chlorine produces the saturated chloride, such as ethylene dichloride from ethylene.



Chlorine reacts with carbon disulfide forming carbon tetrachloride by replacement of sulfur.



Chlorine (or its aqueous solution) will displace bromine or iodine from their metallic binary compounds. With cyanides and thiocyanates (see Cyanides), chlorine reacts to form cyanogen chloride and thiocyanogen chloride.



Chlorine dissolves in water (maximum solubility about 1% at 9.6°C) forming an equilibrium mixture containing hypochlorous acid, HClO ,



Observation of this equilibrium indicates why high pH favors shifting toward the right and increased acidity will tend to drive the reaction to the left.

In hypochlorous acid and hypochlorites, chlorine exhibits the oxidation number +1, with the oxidation numbers +3, +5, and +7 being illustrated by the compounds sodium chlorite, NaClO_2 , sodium chlorate, NaClO_3 , and sodium perchlorate, NaClO_4 . All of these compounds are of commercial importance and are discussed under Chlorine oxygen acids. The oxidation-reduction potentials of chlorine in these oxidation states, in acidic and basic solutions, appear below.

Oxidation number	Reaction	Volts at 25°C
-1	$\text{Cl}^- \rightleftharpoons \frac{1}{2} \text{Cl}_2 + e$	-1.358
+1 acidic	$\frac{1}{2} \text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HClO} + e$	-1.63
+3 acidic	$\frac{1}{2} \text{Cl}_2 + 2 \text{H}_2\text{O} \rightleftharpoons 3 \text{H}^+ + \text{HClO}_2 + 3 e$	-1.63
+5 acidic	$\frac{1}{2} \text{Cl}_2 + 3 \text{H}_2\text{O} \rightleftharpoons 6 \text{H}^+ + \text{ClO}_3^- + 5 e$	-1.47
+7 acidic	$\frac{1}{2} \text{Cl}_2 + 4 \text{H}_2\text{O} \rightleftharpoons 8 \text{H}^+ + \text{ClO}_4^- + 7 e$	-1.34
+1 basic	$\text{Cl}^- + 2 \text{OH}^- \rightleftharpoons \text{ClO}^- + \text{H}_2\text{O} + 2 e$	-0.94
+3 basic	$\text{Cl}^- + 4 \text{OH}^- \rightleftharpoons \text{ClO}_2^- + 2 \text{H}_2\text{O} + 4 e$	-0.76
+5 basic	$\text{Cl}^- + 6 \text{OH}^- \rightleftharpoons \text{ClO}_3^- + 3 \text{H}_2\text{O} + 6 e$	-0.62
+7 basic	$\text{Cl}^- + 8 \text{OH}^- \rightleftharpoons \text{ClO}_4^- + 4 \text{H}_2\text{O} + 8 e$	-0.51

Chlorine does not react directly with oxygen although the following oxides have been described in the chemical literature: Cl_2O , ClO_2 , ClO_3 , and Cl_2O_7 . All are characterized as being unstable, decomposing with varying degrees of explosive violence.

Chlorine monoxide (hypochlorous anhydride), Cl_2O , is pale orange-yellow with a slight greenish tinge, having an odor similar to that of chlorine. It is prepared by passing chlorine over cooled precipitated mercuric oxide,



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or by distilling a fairly concentrated solution of hypochlorous acid at low pressure. Chlorine monoxide explodes readily, but not violently, on heating. It may be distilled in the absence of organic matter. It is a strong oxidizing agent and will convert most metals into a mixture of oxides and chlorides. Its composition is given by the reaction taking place in its explosion upon heating,



and subsequent absorption of the chlorine by potassium hydroxide. Contact of chlorine monoxide with oxidizable materials such as paper, sulfur, phosphorus, or carbonaceous compounds results in explosive reactions forming oxychlorides or oxides and chlorides of the reacting elements.

Chlorine dioxide, ClO_2 , is a reddish-yellow unstable gas with an unpleasant odor, which is extremely soluble in water. Its hydrate $\text{ClO}_2 \cdot 6\text{H}_2\text{O}$ is crystalline yellow and stable up to 18°C . The aqueous solution is stable in the dark. The gas explodes on the smallest provocation. Chlorine dioxide may be prepared by any of the following means: (a) by action of chlorine on silver chlorate,



(b) by reaction of potassium chlorate by disproportionation on treatment with sulfuric acid,



(c) by reaction of potassium chlorate with oxalic acid,



or (d) by the reaction of chlorine gas on sodium chlorite,



Chlorine dioxide dissolves in potassium hydroxide solution according to the following reaction:



The preparation of ClO_2 by the action of chlorine on sodium chlorite is an important industrial process (see Chlorites under Chlorine oxygen acids).

Chlorine trioxide, ClO_3 , is prepared by the action of chlorine dioxide on ozone. When the mixed gases are cooled with ice, brown drops of a solution of chlorine dioxide in chlorine trioxide are formed. The chlorine dioxide is removed by distillation at low pressure.

Chlorine trioxide decomposes even at 0°C to a mixture of other oxides of chlorine and ultimately to oxygen and chlorine. If it is mixed with water vapor and cooled, it yields a mixture of chloric acid and perchloric acid,



but an explosion occurs if it is added to water. In the liquid state ClO_3 exhibits the dimeric formula Cl_2O_6 .

If phosphorus pentoxide is added to anhydrous or highly concentrated perchloric acid below 0°C , the anhydride of perchloric acid, Cl_2O_7 , is produced,



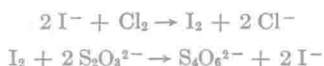
Also, if potassium perchlorate is heated with chlorosulfonic acid, HOClSO_2 , under reduced pressure, a good yield of Cl_2O_7 is obtained, but the chlorine heptoxide produced is contaminated with sulfur compounds.

Chlorine heptoxide explodes when struck or when in contact with a flame. It has no action in the cold with sulfur, wood, or paper but explodes on contact with iodine. Raman spectra of Cl_2O_7 indicate that the molecule consists of two ClO_3 groups linked by an oxygen atom. It is the anhydride of perchloric acid.

Analysis

The odor of elemental chlorine serves to reveal its presence in very low concentrations, but a more specific test is based upon its property of liberating iodine from aqueous potassium iodide. This test can be made more sensitive by the addition of a few drops of carbon tetrachloride or carbon disulfide to the reaction vessel. Upon shaking, the liberated iodine dissolves in the added solvent giving a violet or pinkish-purple tint. If potassium bromide is used in place of the iodide, the chlorine liberates bromine, which dissolves in the added heavy liquid layer, producing a yellowish-brown color.

Elementary chlorine can be estimated by indirect titration using sodium thiosulfate. Direct titration is not possible, as chlorine oxidizes the thiosulfate practically quantitatively to the sulfate. The solution containing the free chlorine is therefore treated with an excess of aqueous potassium iodide and the liberated iodine is then titrated with standard thiosulfate solution. The reactions taking place may be represented by the following equations:



Certain of the oxysalts of chlorine such as hypochlorite or chlorite will also liberate iodine from iodide in acid solution. Thus any quantitative test for elemental chlorine should be conducted following suitable negative qualitative tests in the material to be examined for such ions as chlorite and hypochlorite.

Chlorine, as chloride, may be detected qualitatively as a white, curdy precipitate formed upon addition of silver nitrate solution to the solution under study. This curdy precipitate is insoluble in nitric acid, but dissolves readily in excess ammonia water, forming the complex silver ammine ion $[\text{Ag}(\text{NH}_3)_2]^+$. Since the presence of the thiocyanate ion will give similar reactions, this ion must be tested for, and removed, if present, prior to the test for the chloride ion. Bromide and iodide ions will form cream to pale yellow curdy precipitates with silver nitrate solution. Both of these silver salts are insoluble in nitric acid, but differ from silver chloride in that silver bromide is but slightly soluble and silver iodide is insoluble in dilute water solutions of ammonia.

Chlorine, as chloride, may be determined gravimetrically by precipitating silver chloride from a dilute nitric acid solution. After washing, this precipitate is carefully dried (not ignited) at a temperature approximating 100°C .

Volumetric methods for determining chloride ion include (1) Volhard method, (2) Mohr method, or (3) use of adsorption indicators.

In the Volhard method, an excess (known volume) of standard silver nitrate is added to the slightly acidified (nitric acid) solution of the chloride. The excess silver ion present is then back-titrated with a standard solution of ammonium thiocyanate using a few drops of ferric sulfate solution as indicator. The presence of a pale