

= Acetic acid =

Acetic acid / *si'tk* / , systematically named ethanoic acid / *no'tk* / , is a colourless liquid organic compound with the chemical formula CH_3COOH (also written as $\text{CH}_3\text{CO}_2\text{H}$ or $\text{C}_2\text{H}_4\text{O}_2$) . When undiluted , it is sometimes called glacial acetic acid . Vinegar is roughly 3 % 9 % acetic acid by volume , making acetic acid the main component of vinegar apart from water . Acetic acid has a distinctive sour taste and pungent smell . In addition to household vinegar , it is mainly produced as a precursor to polyvinyl acetate and cellulose acetate . Although it is classified as a weak acid , concentrated acetic acid is corrosive and can attack the skin .

Acetic acid is the second simplest carboxylic acid (after formic acid) and consists of two small functional groups , an acetyl group (sometimes symbolized as Ac) and a hydroxyl group (AcOH) ; it can also be viewed as a methyl group and a carboxyl group linked . It is an important chemical reagent and industrial chemical , used primarily in the production of cellulose acetate for photographic film , polyvinyl acetate for wood glue , and synthetic fibres and fabrics . In households , diluted acetic acid is often used in descaling agents . In the food industry , acetic acid is controlled by the food additive code E260 as an acidity regulator and as a condiment . As a food additive it is approved for usage in many countries , including Canada , the European Union , the United States , Australia and New Zealand . In biochemistry , the acetyl group , derived from acetic acid , is fundamental to all forms of life . When bound to coenzyme A , it is central to the metabolism of carbohydrates and fats .

The global demand for acetic acid is about 6 @. 5 million metric tons per year (Mt / a) , of which approximately 1 @. 5 Mt / a is met by recycling ; the remainder is manufactured from petrochemical feedstock . As a chemical reagent , biological sources of acetic acid are of interest , but generally cannot compete economically . Vinegar is dilute acetic acid , often produced by fermentation and subsequent oxidation of ethanol .

= = Nomenclature = =

The trivial name acetic acid is the most commonly used and preferred IUPAC name . The systematic name ethanoic acid , a valid IUPAC name , is constructed according to the substitutive nomenclature . The name acetic acid derives from acetum , the Latin word for vinegar , and is related to the word acid itself .

Glacial acetic acid is a name for water @-@ free (anhydrous) acetic acid . Similar to the German name Eisessig (ice @-@ vinegar) , the name comes from the ice @-@ like crystals that form slightly below room temperature at 16 @. 6 ° C (61 @. 9 ° F) (the presence of 0 @. 1 % water lowers its melting point by 0 @. 2 ° C) .

A common abbreviation for acetic acid is AcOH , where Ac stands for the acetyl group $\text{CH}_3\text{C}(=\text{O})$. Acetate (CH_3COO^-) is abbreviated AcO^- . The Ac is not to be confused with the abbreviation for the chemical element actinium . To better reflect its structure , acetic acid is often written as $\text{CH}_3\text{C}(\text{O})\text{OH}$, $\text{CH}_3\text{C}(=\text{O})\text{OH}$, CH_3COOH , and $\text{CH}_3\text{CO}_2\text{H}$.

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= = Properties = =

= = = Acidity = = =

The hydrogen centre in the carboxyl group (COOH) in carboxylic acids such as acetic acid can separate from the molecule by ionization :



Because of this release of the proton (H^+), acetic acid has acidic character . Acetic acid is a weak monoprotic acid . In aqueous solution , it has a pK_a value of 4 . Its conjugate base is acetate (CH_3COO^-) . A 1 M solution (about the concentration of domestic vinegar) has a pH of 2 . 4 , indicating that merely 0 . 4 % of the acetic acid molecules are dissociated .

== Structure ==

In solid acetic acid , the molecules form pairs (dimers) , being connected by hydrogen bonds . The dimers can also be detected in the vapour at 120°C (248°F) . Dimers also occur in the liquid phase in dilute solutions in non hydrogen bonding solvents , and a certain extent in pure acetic acid , but are disrupted by hydrogen bonding solvents . The dissociation enthalpy of the dimer is estimated at 65 . 66 kJ / mol , and the dissociation entropy at 154 . 157 J mol⁻¹ K⁻¹ . Other lower carboxylic acids dimerize in a similar fashion .

== Solvent properties ==

Liquid acetic acid is a hydrophilic (polar) protic solvent , similar to ethanol and water . With a moderate relative static permittivity (dielectric constant) of 6 . 2 , it dissolves not only polar compounds such as inorganic salts and sugars , but also non polar compounds such as oils and elements such as sulfur and iodine . It readily mixes with other polar and non polar solvents such as water , chloroform , and hexane . With higher alkanes (starting with octane) , acetic acid is not completely miscible , and its miscibility declines with longer n alkanes . The solvent and miscibility properties of acetic acid make it a useful industrial chemical , for example , as a solvent in the production of dimethyl terephthalate .

== Biochemistry ==

At physiological pHs , acetic acid is usually fully ionised to acetate . The acetyl group , derived from acetic acid , is fundamental to all forms of life . When bound to coenzyme A , it is central to the metabolism of carbohydrates and fats . Unlike longer chain carboxylic acids (the fatty acids) , acetic acid does not occur in natural triglycerides . However , the artificial triglyceride triacetin (glycerine triacetate) is a common food additive and is found in cosmetics and topical medicines .

Acetic acid is produced and excreted by acetic acid bacteria , notably the *Acetobacter* genus and *Clostridium acetobutylicum* . These bacteria are found universally in foodstuffs , water , and soil , and acetic acid is produced naturally as fruits and other foods spoil . Acetic acid is also a component of the vaginal lubrication of humans and other primates , where it appears to serve as a mild antibacterial agent .

== Production ==

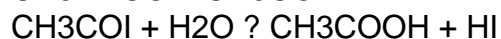
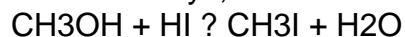
Acetic acid is produced industrially both synthetically and by bacterial fermentation . About 75 % of acetic acid made for use in the chemical industry is made by the carbonylation of methanol , explained below . The biological route accounts for only about 10 % of world production , but it remains important for the production of vinegar because many food purity laws require vinegar used in foods to be of biological origin . As of 2003 - 2005 , total worldwide production of virgin acetic acid was estimated at 5 Mt / a (million tonnes per year) , approximately half of which was produced in the United States . European production was approximately 1 Mt / a and declining , while Japanese production was 0 . 7 Mt / a . Another 1 . 5 Mt were recycled each year , bringing the total world market to 6 . 5 Mt / a . Since then the global production has increased to 10

@. @ 7 Mt / a (in 2010) , and further ; however , a slowing in this increase in production is predicted . The two biggest producers of virgin acetic acid are Celanese and BP Chemicals . Other major producers include Millennium Chemicals , Sterling Chemicals , Samsung , Eastman , and Svensk Etanolkemi .

== Methanol carbonylation ==

Most acetic acid is produced by methanol carbonylation . In this process , methanol and carbon monoxide react to produce acetic acid according to the equation :

The process involves iodomethane as an intermediate , and occurs in three steps . A catalyst , metal carbonyl , is needed for the carbonylation (step 2) .



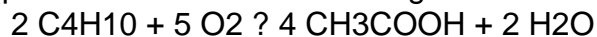
Two related processes for the carbonylation of methanol : the rhodium @-@ catalyzed Monsanto process , and the iridium @-@ catalyzed Cativa process . The latter process is greener and more efficient and has largely supplanted the former process , often in the same production plants . Catalytic amounts of water are used in both processes , but the Cativa process requires less , so the water @-@ gas shift reaction is suppressed , and fewer by @-@ products are formed .

By altering the process conditions , acetic anhydride may also be produced on the same plant using the rhodium catalysts .

== Acetaldehyde oxidation ==

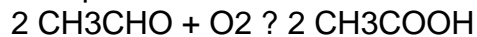
Prior to the commercialization of the Monsanto process , most acetic acid was produced by oxidation of acetaldehyde . This remains the second @-@ most @-@ important manufacturing method , although it is usually not competitive with the carbonylation of methanol .

The acetaldehyde may be produced by oxidation of butane or light naphtha , or by hydration of ethylene . When butane or light naphtha is heated with air in the presence of various metal ions , including those of manganese , cobalt , and chromium , peroxides form and then decompose to produce acetic acid according to the chemical equation :



The typical reaction is conducted at temperatures and pressures designed to be as hot as possible while still keeping the butane a liquid . Typical reaction conditions are 150 ° C (302 ° F) and 55 atm . Side @-@ products may also form , including butanone , ethyl acetate , formic acid , and propionic acid . These side @-@ products are also commercially valuable , and the reaction conditions may be altered to produce more of them where needed . However , the separation of acetic acid from these by @-@ products adds to the cost of the process .

Under similar conditions and using similar catalysts as are used for butane oxidation , the oxygen in air to produce acetic acid can oxidize acetaldehyde .



Using modern catalysts , this reaction can have an acetic acid yield greater than 95 % . The major side @-@ products are ethyl acetate , formic acid , and formaldehyde , all of which have lower boiling points than acetic acid and are readily separated by distillation .

== Ethylene oxidation ==

Acetaldehyde may be prepared from ethylene via the Wacker process , and then oxidised as above . In more recent times , chemical company Showa Denko , which opened an ethylene oxidation plant in ?ita , Japan , in 1997 , commercialised a cheaper single @-@ stage conversion of ethylene to acetic acid . The process is catalyzed by a palladium metal catalyst supported on a heteropoly acid such as tungstosilicic acid . It is thought to be competitive with methanol carbonylation for smaller plants (100 ? 250 kt / a) , depending on the local price of ethylene . The approach will be

based on utilizing a novel selective photocatalytic oxidation technology for the selective oxidation of ethylene and ethane to acetic acid . Unlike traditional oxidation catalysts , the selective oxidation process will use UV light to produce acetic acid at ambient temperatures and pressure .

= = = Oxidative fermentation = = =

For most of human history , acetic acid bacteria of the genus *Acetobacter* have made acetic acid , in the form of vinegar . Given sufficient oxygen , these bacteria can produce vinegar from a variety of alcoholic foodstuffs . Commonly used feeds include apple cider , wine , and fermented grain , malt , rice , or potato mashes . The overall chemical reaction facilitated by these bacteria is :



A dilute alcohol solution inoculated with *Acetobacter* and kept in a warm , airy place will become vinegar over the course of a few months . Industrial vinegar @-@ making methods accelerate this process by improving the supply of oxygen to the bacteria .

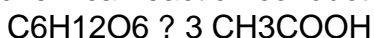
The first batches of vinegar produced by fermentation probably followed errors in the winemaking process . If must is fermented at too high a temperature , *acetobacter* will overwhelm the yeast naturally occurring on the grapes . As the demand for vinegar for culinary , medical , and sanitary purposes increased , vintners quickly learned to use other organic materials to produce vinegar in the hot summer months before the grapes were ripe and ready for processing into wine . This method was slow , however , and not always successful , as the vintners did not understand the process .

One of the first modern commercial processes was the " fast method " or " German method " , first practised in Germany in 1823 . In this process , fermentation takes place in a tower packed with wood shavings or charcoal . The alcohol @-@ containing feed is trickled into the top of the tower , and fresh air supplied from the bottom by either natural or forced convection . The improved air supply in this process cut the time to prepare vinegar from months to weeks .

Nowadays , most vinegar is made in submerged tank culture , first described in 1949 by Otto Hromatka and Heinrich Ebner . In this method , alcohol is fermented to vinegar in a continuously stirred tank , and oxygen is supplied by bubbling air through the solution . Using modern applications of this method , vinegar of 15 % acetic acid can be prepared in only 24 hours in batch process , even 20 % in 60 @-@ hour fed @-@ batch process .

= = = Anaerobic fermentation = = =

Species of anaerobic bacteria , including members of the genus *Clostridium* or *Acetobacterium* can convert sugars to acetic acid directly without creating ethanol as an intermediate . The overall chemical reaction conducted by these bacteria may be represented as :



These acetogenic bacteria produce acetic acid from one @-@ carbon compounds , including methanol , carbon monoxide , or a mixture of carbon dioxide and hydrogen :



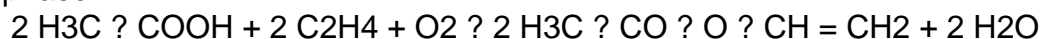
This ability of *Clostridium* to metabolize sugars directly , or to produce acetic acid from less costly inputs , suggests that these bacteria could produce acetic acid more efficiently than ethanol @-@ oxidizers like *Acetobacter* . However , *Clostridium* bacteria are less acid @-@ tolerant than *Acetobacter* . Even the most acid @-@ tolerant *Clostridium* strains can produce vinegar in concentrations of only a few per cent , compared to *Acetobacter* strains that can produce vinegar in concentrations up to 20 % . At present , it remains more cost @-@ effective to produce vinegar using *Acetobacter* , rather than using *Clostridium* and concentrating it . As a result , although acetogenic bacteria have been known since 1940 , their industrial use is confined to a few niche applications .

= = Uses = =

Acetic acid is a chemical reagent for the production of chemical compounds . The largest single use of acetic acid is in the production of vinyl acetate monomer , closely followed by acetic anhydride and ester production . The volume of acetic acid used in vinegar is comparatively small .

== Vinyl acetate monomer ==

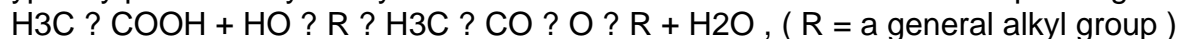
The primary use of acetic acid is the production of vinyl acetate monomer (VAM) . In 2008 , this application was estimated to consume a third of the world 's production of acetic acid . The reaction consists of ethylene and acetic acid with oxygen over a palladium catalyst , conducted in the gas phase .



Vinyl acetate can be polymerised to polyvinyl acetate or other polymers , which are components in paints and adhesives .

== Ester production ==

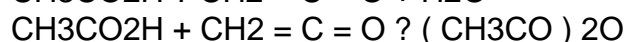
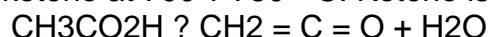
The major esters of acetic acid are commonly used as solvents for inks , paints and coatings . The esters include ethyl acetate , n -butyl acetate , isobutyl acetate , and propyl acetate . They are typically produced by catalyzed reaction from acetic acid and the corresponding alcohol :



Most acetate esters , however , are produced from acetaldehyde using the Tishchenko reaction . In addition , ether acetates are used as solvents for nitrocellulose , acrylic lacquers , varnish removers , and wood stains . First , glycol monoethers are produced from ethylene oxide or propylene oxide with alcohol , which are then esterified with acetic acid . The three major products are ethylene glycol monoethyl ether acetate (EEA) , ethylene glycol monobutyl ether acetate (EBA) , and propylene glycol monomethyl ether acetate (PMA , more commonly known as PGMEA in semiconductor manufacturing processes , where it is used as a resist solvent) . This application consumes about 15 % to 20 % of worldwide acetic acid . Ether acetates , for example EEA , have been shown to be harmful to human reproduction .

== Acetic anhydride ==

The product of the condensation of two molecules of acetic acid is acetic anhydride . The worldwide production of acetic anhydride is a major application , and uses approximately 25 % to 30 % of the global production of acetic acid . The main process involves dehydration of acetic acid to give ketene at 700 ? 750 ° C. Ketene is thereafter reacted with acetic acid to obtain the anhydride :



Acetic anhydride is an acetylation agent . As such , its major application is for cellulose acetate , a synthetic textile also used for photographic film . Acetic anhydride is also a reagent for the production of heroin and other compounds .

== Use as solvent ==

Glacial acetic acid is an excellent polar protic solvent , as noted above . It is frequently used as a solvent for recrystallization to purify organic compounds . Acetic acid is used as a solvent in the production of terephthalic acid (TPA) , the raw material for polyethylene terephthalate (PET) . In 2006 , about 20 % of acetic acid was used for TPA production .

Acetic acid is often used as a solvent for reactions involving carbocations , such as Friedel -Crafts alkylation . For example , one stage in the commercial manufacture of synthetic camphor involves a Wagner -Meerwein rearrangement of camphene to isobornyl acetate ; here acetic acid acts both as a solvent and as a nucleophile to trap the rearranged carbocation .

Glacial acetic acid is used in analytical chemistry for the estimation of weakly alkaline substances

such as organic amides . Glacial acetic acid is a much weaker base than water , so the amide behaves as a strong base in this medium . It then can be titrated using a solution in glacial acetic acid of a very strong acid , such as perchloric acid .

=== Medical use ===

Diluted acetic acid is used in physical therapy using iontophoresis .

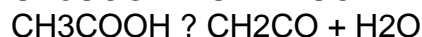
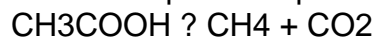
=== Vinegar ===

Vinegar is typically 4 ? 18 % acetic acid by mass . Vinegar is used directly as a condiment , and in the pickling of vegetables and other foods . Table vinegar tends to be more diluted (4 % to 8 % acetic acid) , while commercial food pickling employs solutions that are more concentrated . The amount of acetic acid used as vinegar on a worldwide scale is not large , but is by far the oldest and best @-@ known application .

=== Reactions ===

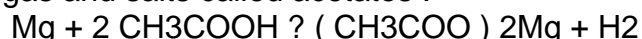
=== Organic chemistry ===

Acetic acid undergoes the typical chemical reactions of a carboxylic acid . Upon treatment with a standard base , it converts to metal acetate and water . With strong bases (e.g. , organolithium reagents) , it can be doubly deprotonated to give $\text{LiCH}_2\text{CO}_2\text{Li}$. Reduction of acetic acid gives ethanol . The OH group is the main site of reaction , as illustrated by the conversion of acetic acid to acetyl chloride . Other substitution derivatives include acetic anhydride ; this anhydride is produced by loss of water from two molecules of acetic acid . Esters of acetic acid can likewise be formed via Fischer esterification , and amides can be formed . When heated above 440°C (824°F) , acetic acid decomposes to produce carbon dioxide and methane , or to produce ketene and water :



=== Reactions with inorganic compounds ===

Acetic acid is mildly corrosive to metals including iron , magnesium , and zinc , forming hydrogen gas and salts called acetates :



Because aluminium forms a passivating acid @-@ resistant film of aluminium oxide , aluminium tanks are used to transport acetic acid . Metal acetates can also be prepared from acetic acid and an appropriate base , as in the popular " baking soda + vinegar " reaction :



A colour reaction for salts of acetic acid is iron (III) chloride solution , which results in a deeply red colour that disappears after acidification . A more sensitive test uses lanthanum nitrate with iodine and ammonia to give a blue solution . Acetates when heated with arsenic trioxide form cacodyl oxide , which can be detected by its malodorous vapours .

=== Other derivatives ===

Organic or inorganic salts are produced from acetic acid , including :

Sodium acetate , used in the textile industry and as a food preservative (E262) .

Copper (II) acetate , used as a pigment and a fungicide .

Aluminium acetate and iron (II) acetate ? used as mordants for dyes .

Palladium (II) acetate , used as a catalyst for organic coupling reactions such as the Heck reaction

Silver acetate , used as a pesticide .

Substituted acetic acids produced include :

Chloroacetic acid (monochloroacetic acid , MCA) , dichloroacetic acid (considered a by @-@ product) , and trichloroacetic acid . MCA is used in the manufacture of indigo dye .

Bromoacetic acid , which is esterified to produce the reagent ethyl bromoacetate .

Trifluoroacetic acid , which is a common reagent in organic synthesis .

Amounts of acetic acid used in these other applications together (apart from TPA) account for another 5 ? 10 % of acetic acid use worldwide . These applications are , however , not expected to grow as much as TPA production .

= = History = =

Vinegar was known early in civilization as the natural result of exposure of beer and wine to air , because acetic acid @-@ producing bacteria are present globally . The use of acetic acid in alchemy extends into the 3rd century BC , when the Greek philosopher Theophrastus described how vinegar acted on metals to produce pigments useful in art , including white lead (lead carbonate) and verdigris , a green mixture of copper salts including copper (II) acetate . Ancient Romans boiled soured wine to produce a highly sweet syrup called sapa . Sapa that was produced in lead pots was rich in lead acetate , a sweet substance also called sugar of lead or sugar of Saturn , which contributed to lead poisoning among the Roman aristocracy .

In the 16th @-@ century German alchemist Andreas Libavius described the production of acetone from the dry distillation of lead acetate , ketonic decarboxylation . The presence of water in vinegar has such a profound effect on acetic acid 's properties that for centuries chemists believed that glacial acetic acid and the acid found in vinegar were two different substances . French chemist Pierre Adet proved them identical .

In 1845 German chemist Hermann Kolbe synthesised acetic acid from inorganic compounds for the first time . This reaction sequence consisted of chlorination of carbon disulfide to carbon tetrachloride , followed by pyrolysis to tetrachloroethylene and aqueous chlorination to trichloroacetic acid , and concluded with electrolytic reduction to acetic acid .

By 1910 , most glacial acetic acid was obtained from the pyroligneous liquor , a product of the distillation of wood . The acetic acid was isolated by treatment with milk of lime , and the resulting calcium acetate was then acidified with sulfuric acid to recover acetic acid . At that time , Germany was producing 10 @, @ 000 tons of glacial acetic acid , around 30 % of which was used for the manufacture of indigo dye .

Because both methanol and carbon monoxide are commodity raw materials , methanol carbonylation long appeared to be attractive precursors to acetic acid . Henri Dreyfus at British Celanese developed a methanol carbonylation pilot plant as early as 1925 . However , a lack of practical materials that could contain the corrosive reaction mixture at the high pressures needed (200 atm or more) discouraged commercialization of these routes . The first commercial methanol carbonylation process , which used a cobalt catalyst , was developed by German chemical company BASF in 1963 . In 1968 , a rhodium @-@ based catalyst (cis ? [Rh (CO) ₂ I₂] ?) was discovered that could operate efficiently at lower pressure with almost no by @-@ products . US chemical company Monsanto Company built the first plant using this catalyst in 1970 , and rhodium @-@ catalyzed methanol carbonylation became the dominant method of acetic acid production (see Monsanto process) . In the late 1990s , the chemicals company BP Chemicals commercialised the Cativa catalyst ([Ir (CO) ₂ I₂] ?) , which is promoted by iridium for greater efficiency . This iridium @-@ catalyzed Cativa process is greener and more efficient and has largely supplanted the Monsanto process , often in the same production plants .

= = = In the interstellar medium = = =

Interstellar acetic acid was discovered in 1996 by a team led by David Mehringer using the former

Berkeley @-@ Illinois @-@ Maryland Association array at the Hat Creek Radio Observatory and the former Millimeter Array located at the Owens Valley Radio Observatory . It was first detected in the Sagittarius B2 North molecular cloud (also known as the Sgr B2 Large Molecule Heimat source) . Acetic acid has the distinction of being the first molecule discovered in the interstellar medium using solely radio interferometers ; in all previous ISM molecular discoveries made in the millimetre and centimetre wavelength regimes , single dish radio telescopes were at least partly responsible for the detections .

= = Health effects and safety = =

Concentrated acetic acid is corrosive to skin and must therefore be handled with appropriate care to avoid skin burns , permanent eye damage , and irritation to the mucous membranes . These burns or blisters may not appear until hours after exposure . Latex gloves offer no protection , so specially resistant gloves , such as those made of nitrile rubber , are worn when handling the compound .

Prolonged skin contact with glacial acetic acid may result in tissue destruction . Inhalation exposure (eight hours) to acetic acid vapours at 10 ppm can produce some irritation of eyes , nose , and throat ; at 100 ppm marked lung irritation and possible damage to lungs , eyes , and skin may result . Vapour concentrations of 1 @, @ 000 ppm cause marked irritation of eyes , nose and upper respiratory tract and cannot be tolerated . These predictions were based on animal experiments and industrial exposure . Skin sensitization to acetic acid is rare , but has occurred .

It has been reported that , in 12 workers exposed for two or more years to acetic acid airborne average concentration of 51 ppm (estimated) , produced symptoms of conjunctive irritation , upper respiratory tract irritation , and hyperkeratotic dermatitis . Exposure to 50 ppm or more is intolerable to most persons and results in intensive lacrimation and irritation of the eyes , nose , and throat , with pharyngeal oedema and chronic bronchitis . Unacclimatised humans experience extreme eye and nasal irritation at concentrations in excess of 25 ppm , and conjunctivitis from concentrations below 10 ppm has been reported . In a study of five workers exposed for seven to 12 years to concentrations of 80 to 200 ppm at peaks , the principal findings were blackening and hyperkeratosis of the skin of the hands , conjunctivitis (but no corneal damage) , bronchitis and pharyngitis , and erosion of the exposed teeth (incisors and canines) .

The hazards of solutions of acetic acid depend on the concentration . The following table lists the EU classification of acetic acid solutions :

Solutions at more than 25 % acetic acid are handled in a fume hood because of the pungent , corrosive vapour . Dilute acetic acid , in the form of vinegar , is practically harmless . However , ingestion of stronger solutions is dangerous to human and animal life . It can cause severe damage to the digestive system , and a potentially lethal change in the acidity of the blood .

Due to incompatibilities , it is recommended to keep acetic acid away from chromic acid , ethylene glycol , nitric acid , perchloric acid , permanganates , peroxides and hydroxyls .

Concentrated acetic acid can be ignited only with difficulty in the laboratory , but becomes a flammable risk in ambient temperatures above 39 ° C (102 ° F) , and can form explosive mixtures with air at higher temperatures (explosive limits : 5 @. @ 4 ? 16 %) .