

How to make Potassium Perchlorate

Potassium Perchlorate has no known hydrates and is not hygroscopic.

Potassium Perchlorate is usually made by double decomposition of Potassium Chloride (KCL) and Sodium Perchlorate (NaClO_4). The Potassium Perchlorate is not very soluble and will precipitate out immediately as a very fine crystalline product (your solution will look like yogurt if you add the KCL quickly) as soon as you add the KCL to the Sodium Perchlorate. The process is as follows: Take a quantity of Sodium Perchlorate solution and add an equal amount of Potassium Chloride solution to it. The precipitate will form immediately. The remaining solution is a Sodium Chloride solution that can be collected and added to a Sodium Perchlorate cell.

The solutions of NaClO_4 and KCL should be neutral for the preceding reaction. If they are not you should neutralize them by adding a small amount of KOH or NaOH. If you don't do this small traces of acid are introduced into the final product which is very dangerous.

You can also make Potassium Perchlorate by decomposition of Potassium Chlorate, it is quite a good way to make the stuff and it will not be contaminated with Potassium Chlorate so long as you heat to the correct temperature. The Potassium Chloride (byproduct) will be fairly easy to get out of the Perchlorate.

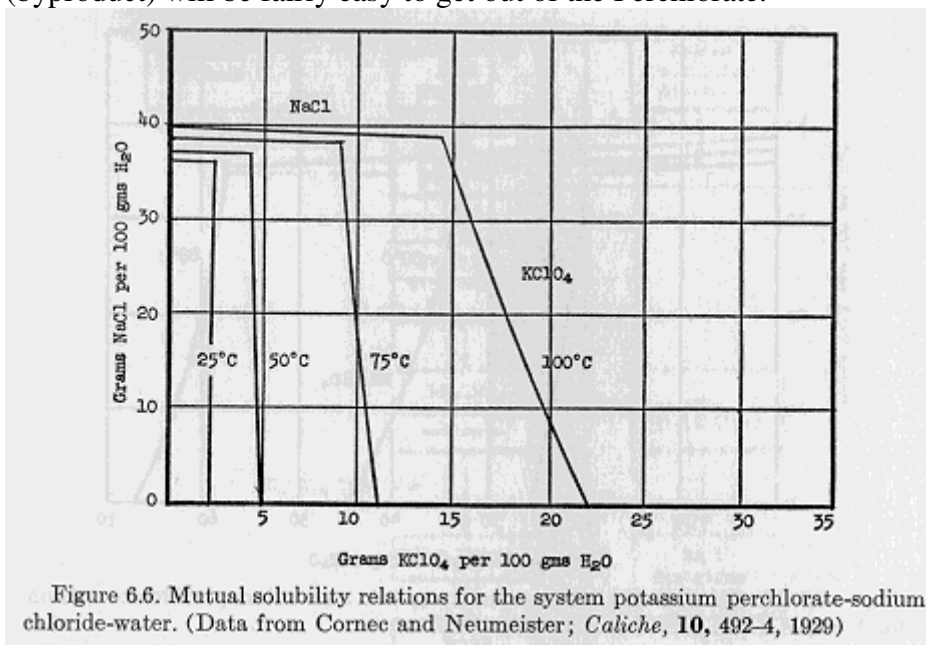
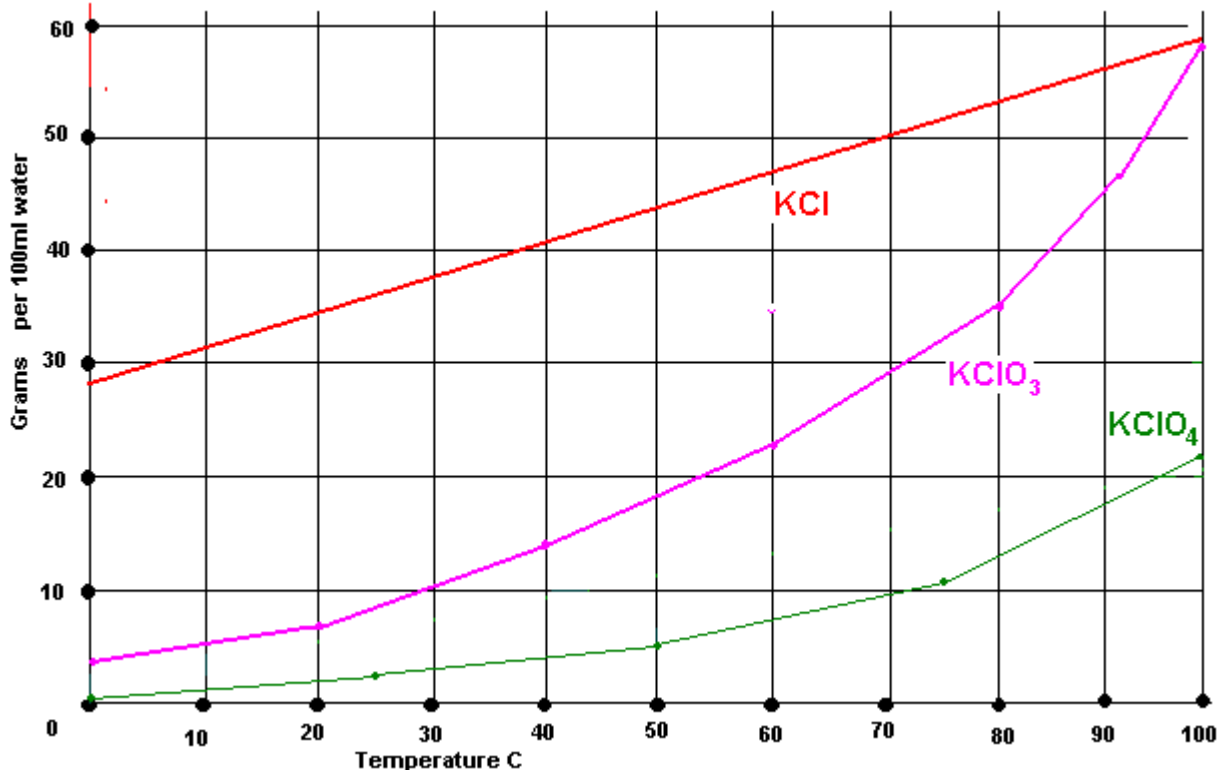


Figure 6.6. Mutual solubility relations for the system potassium perchlorate-sodium chloride-water. (Data from Cornec and Neumeister; *Caliche*, 10, 492-4, 1929)

Potassium Perchlorate can also be made by electrolyzing Potassium Chlorate in a similar manner to that used for Sodium Chlorate. The solubility of Potassium Chlorate is low and the concentration of Chlorate in the cell will be low and you will have to use large volumes of solution if you want large weights of product. You will also get lower current efficiency, the Perchlorate will precipitate out as it is formed and may even encrust the anode. You will have to be careful and make sure that your finished product has all Chlorate removed. There is not much information regarding the manufacture of K

Perchlorate via electro synthesis in the literature. Some have suggested that it is erosive on Lead Dioxide anodes but this is not confirmed.



Some useful data				
	KCl	KClO ₄	NaCl	NaClO ₄
Molecular weight	74.5	138.5	58.5	122.5

Other compounds may be used instead of KCL, for example K sulfate and K Nitrate but if you use the Chloride the by product is Sodium Chloride (NaCL) which can be fed back into the recrystallizing stage. It is better to feed back this solution to the recrystallization stage as opposed to the Sodium Chlorate cell. If you feed it back to the cell you may get K Chlorate being precipitated and it is hard to clean up the discolored K Chlorate. It is not critical though.

Destroying Chlorate with chemicals

When making Perchlorates from Sodium Perchlorate you must have pure Perchlorate. The only sensible and feasible way to purify Sodium Perchlorate from Chlorate contamination is to destroy all traces of Chlorate by chemical treatment. When 'raw' Sodium Perchlorate is removed from cell liquor it will be contaminated with some Chlorate. There must not be too much Chlorate in the product or it will be wasteful and foolish to attempt to destroy a large amount of Chlorate by chemicals.

The Perchlorate should be dried and weighed and then re dissolved so you can then destroy all traces of Chlorate before going on to make other Perchlorates. If you have a solution of Perchlorate that has been obtained by letting your cell run for long enough to convert nearly all of the Chlorate to Perchlorate then you can proceed with the destruction of the Chlorate without crystallizing out the Perchlorate. The absence of Chlorates should be checked for by using a sensitive test for Chlorate after the destruction step has been completed. See [Tests for Chlorate and Perchlorate](#). There should be NO Chlorate. A Perchlorate that contains ANY Chlorate must be treated as if it WAS Chlorate in regard to dangerous combinations with combustibles, like for example Sulfur. You also have the extra problem of Chlorate contamination if you are going to make Ammonium Perchlorate, you don't want any Ammonium Chlorate forming.

Note: Sulphite can be spelled either as said or as Sulfite.
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Chemicals for the destruction of Chlorate	
Chemical	Comments
Sodium Metabisulphite $\text{Na}_2\text{S}_2\text{O}_5$	Also called di-Sodium Disulphite or Sodium Disulphite or Sodium Pyrosulphite. This can be got at the local wine making store in the form of 'Campden tables' where it is used in wine making and sterilising. It is used as a food additive, E223. It is similar to Sodium Bisulphite, Metabisulphite being the dehydrated derivative of two molecules of Bisulphite.
Sodium Bisulphite NaHSO_3	Also called Sodium Hydrogen Sulphite. It is used as a food additive, E222.
Sodium Sulphite Na_2SO_3	It is used as a food additive, E221.
Sulphur Dioxide SO_2	Used in US Patent No. 2,392,769. It can be generated by burning sulphur or you can purchase in a cylinder. It is also used as a food preserver and disinfectant. It is a suffocating gas.
Ferrous (II) Sulphate $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ + Sulphuric Acid	Common names are Copras, Iron Sulphate, Green Vitriol. It is use for killing moss in lawns and can be got at the local garden store.
Ferrous Ammonium Sulphate $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ + Sulphuric Acid	Also called di-Ammonium Iron (II) Sulphate. It is somewhat expensive. Similar to Iron (II) Sulphate
Acids	HCl and others. Easy to obtain. You need to be careful of the ClO_2 gas produced.
Heat	The solid product can be heated so that all remaining Chlorate is converted to Perchlorate and Chloride Temperature control need to be accurate and the heating needs to

	be for the required time.
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All the chemicals below work by reducing the Chlorate ion. The sulphites have the same reducing power in dilute acidified solutions as sulphur dioxide. All the sulphite and sulphur dioxide reactions take place in a similar manner. You can test for the presence of Chlorate in your product as per [US Patent No. 2,392,769](#)

Sodium metabisulphite

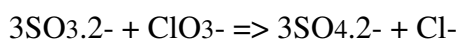
The solution should first be acidified to pH 3 or so using sulphuric or HCl acid. The sulphite added and the solution heated strongly or boiled

The Sodium Metabisulphite reactions take place according to:

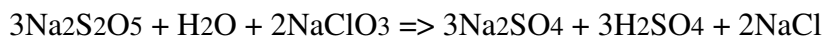
First, the Metabisulphite dissociates:



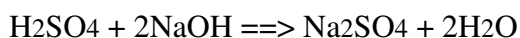
The sulphite then reacts with Chlorate:



The overall reaction is:



You can then neutralize the solution using Sodium Hydroxide which will give you more Sodium Sulphate and water.



Sodium Bisulphite

Similar to Metabisulphite

Sodium Sulphite

Similar to Bisulphite

Sodium Disulfite

Similar to Bisulphite

Sulphur Dioxide

See [US Patent No. 2,392,769](#)

Ferrous Sulphate + H₂SO₄

This is cheap and easy to obtain. The reaction products should not be a problem. The Sulphate should be dissolved in the acidified water (the acid will stop Iron Hydroxide form forming, it is also necessary for the reaction that destroys the Chlorate) first and then added to the solution that is being treated.

Keep the pH below 3 for the reaction to proceed and the solution should be heated/boiled.

Ferrous Ammonium Sulphate + H₂SO₄

Same as Ferrous (II) Sulphate but it is more expensive and harder to get. Does not oxidise in air as Ferrous (II) Sulphate does and won't form Hydroxide when added to water. Keep solution below pH 3 for destruction reaction to proceed. Heating or boiling should be used.

Strong acids

HCl is the best acid to use. Acid is added to the solution to be treated and the solution is boiled. Yellow gas is released (the more Chlorate the more gas) as the Chlorate is destroyed. This gas is ClO₂ and is explosive at concentrations above 10%. It is also very toxic and should not be inhaled under any circumstances. If using HCl, any excess acid can be gotten rid of by boiling. There should not be large amounts of Chlorate present (as with all the other methods) when adding acid. The solution is then basified with NaOH (or appropriate hydroxide or carbonate if you are concerned for the final color that the produce will make when burned) and the presence of Chlorate should be checked for using some of the sensitive tests for Chlorate. HCl acid can be purchased at the builders providers and is used for cleaning cement.

Tests for Chlorate and Perchlorate

The ability to be able to tell what, and how much of what, is in your product is very useful. The ability to test for trace amounts of Chlorate in Perchlorate is particularly useful when it comes to making other Perchlorates from Sodium Perchlorate especially Ammonium Perchlorate as you don't want any Ammonium Chlorate to be formed under any circumstances. The presence of small amount of Chlorate in Perchlorate is OK so long as you are aware of the problems/dangers that it poses. The problems arise when someone thinks that having 99% Perchlorate + 1% Chlorate is similar to having pure Perchlorate. This is not the case.

In order to ascertain how much Chlorate you have in a product you must do a titration. Another way is to destroy all of the Chlorate in the product and weigh the product before and after in order to ascertain how much Chlorate was there in the first place. This will not work if you have Chlorate and Perchlorate together. The following is some very

useful tests that are quick and easy to do. Some of the chemicals will have to be purchased from the Lab supply store. It should be noted that some of the tests below will work better (or it is sometimes essential) if a SOLID sample of what you are testing is added to the reagent. You will have to take out some of the liquid sample and dry it on a watch glass and use the solid obtained, for the test.

Perchlorate tests

Methylene blue

The following test for Perchlorate is very useful when you are making Perchlorate by letting a Chlorate cell run and run until all the Chloride---->Chlorate has been converted to Perchlorate. This test will tell you when Perchlorate has started to form. This usually happens at about 10% Chloride concentration.

Methylene blue is used for staining specimens that are to be examined under a microscope. It may be possible to purchase it in a shop that sells dyes. It is sometimes sold in pet shops as a dilute solution for treating diseases of fish.

A 0.3% solution of Methylene blue is made by dissolving 0.3 grams Methylene blue in 100ml water. When a drop of this is put into a (liquid) sample from a cell that has Perchlorate in it the Methylene blue will form an insoluble purple precipitate. The solution should not be acid, if it is the purple precipitate. will dissolve and you wont see it. The solutions should also be cold (important). It is fairly sensitive and will detect Perchlorate levels at one gram per liter or less. You should add the Methylene blue to the sample to be tested for to see the color change.

Persulphates and Dichromate (cell additives) also give a purple color which is difficult to distinguish from the Perchlorate precipitate. The dilution of these substances will be fairly large and will probably not interfere with the test. Test a sample of your cell at the start of the run in order to see if the Persulphate or Dichromate is causing a purple color. You will then be able to judge an increase in purple color as being caused by Perchlorate formation.

See [here](#) and [here](#) for more info.

Potassium Chloride

This is a very crude and insensitive test. Since Potassium Perchlorate is not very soluble you will get an IMMEDIATE white fine precipitate of K Perchlorate in a solution of Sodium Perchlorate. The Perchlorate concentration will need to be fairly high. The test sample should be as cold as possible to get the best sensitivity. If you are testing a very concentrated solution of Sodium Chlorate for the presence of Perchlorate you may mistake the precipitate of K Chlorate that you may get (since the solution is very concentrated). Dilute your solution a bit so that you are not getting a precipitate of K Chlorate. This test can be difficult to interpret correctly. Make sure you do not confuse the K Chlorate precipitate that you will get with a K Perchlorate precipitate. It generally takes a few seconds for a K Chlorate precipitate to form. K Chlorate forms plates which can be seen reflection light (glinting) when viewed under a strong light. The K

Perchlorate precipitate happens immediately and has very small crystal size with no glinting. Also if you have a solution containing Chlorate + Chloride (no Perchlorate) you may get a precipitate similar to Perchlorate (ie. a fine white precipitate with no crystal glinting).

Using Ethanol instead of water will increase the sensitivity of this test.

This test is not recommended, better to use Methylene blue.

Chlorate tests

N-Phenylanthranilic Acid

See Wouters page or better [here](#).

This will have to be purchased from a lab supply store. It is added to some concentrated sulphuric acid. A red, orange or yellow color indicates the presence of Chlorate in a Perchlorate sample. The test is fairly sensitive.

Mix about 0.1g of the phenylanthranilic acid with about 15cc concentrated Sulphuric acid to give a blackish/blueish solution. Some of the solid sample to be tested is put in the bottom of a small (preferable white) container and a few drops of the reagent added and put in contact with the sample. The colors above will appear if Chlorate is present. Be careful and do not use too much Perchlorate sample because if it contains a lot of Chlorate you may get splattering when the Chlorate reacts violently with the concentrated acid.

You can also use the test by adding the test reagent to a sample of dissolved Perchlorate to be tested. This can be problematic because if the test reagent is made up for a period of time it seems to give a yellow color when added to pure water.

The sensitivity of the test in solutions is thus:

A 0.4 g/l KClO_3 solution gives a just barely visible discoloration. The best is to do the test both on clean water and on the unknown. If you then compare the colors of the precipitates side by side you can spot the yellow color more easily if you are testing low concentrations. For concentrations above 2 g/l or so this is not really necessary. The concentration of the indicator may also make a difference. 26.3 mg phenylanthranilic acid in 2.00 ml of 96% Sulfuric acid was used to prepare the indicator solution used here.

Be careful

A few drops of indicator solution was left over. A tiny bit of solid KClO_3 was dropped into it. Two seconds later a -bang- followed. ClO_2 I guess.

Lesson:

Be careful you don't have pure or nearly pure Chlorate as it will react when it comes into contact with the sulphuric acid.

Aniline Reagent

The Aniline Reagent is made by adding 3.6grams of Aniline to 100ml of 17% HCl acid solution. The 100ml of acid can be made by adding 50ml water to 50ml concentrated

(35%) HCl acid. The 2g sample of solution (use solid for maximum sensitivity) is mixed with about 2ml of the reagent and 0.5ml water added. If Chlorate is plentiful you will get a red color immediately which will turn to dark blue. If Chlorates are only there in smallish amounts, a blue or green color appears within 30 minutes.

A solid sample can be added directly to the reagent and the solid left sitting on the bottom of the container. A blue color will be seen on/at the sample if Chlorate is present.

Note: You can compare the Chlorate content by comparing the color obtained from your test, with the color obtained with solutions of pure Chlorate of known contents. I don't know if colored solutions made up from known Chlorate concentrations will hold there colors for long periods of time. If they do hold their colors for long periods of time, then this test would be a good way to do a "quick and dirty" titration. You would simply have a row of colored bottles for to compare your unknown with.

Aniline Sulphate

A small quantity (less than 0.5g) of the solid is mixed with 1ml of concentrated sulphuric acid and 2-3ml of aqueous aniline sulphate solution added. A deep blue color is obtained if Chlorate is present. Sensitivity of this test is not known.

Indigo Carmine

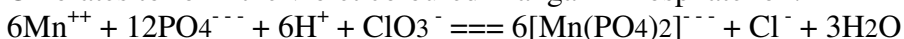
Indigo Carmine is used for microscopical staining (similar to the methylene blue) It will have to be purchased from a lab supply store. It is fairly expensive per gram but you will only need a few grams for to do a lot of tests. This test is used in [US Patent No. 2,392,769](#).

This test is extremely sensitive and will detect Chlorate levels down to parts per million. A stock test indicator solution is made by dissolving one gram of Indigo Carmine per liter water. Tests for Chlorate are made by mixing 1ml of the Indigo Carmine stock test indicator with 5ml of concentrated Hydrochloric acid, and the mixture heated to boiling. To this boiling mixture, 5ml of the cell solution are added. Five parts per million of Chlorate will cause a sharp discoloration of the indicator, and one part per million can be detected. Sulphur Dioxide does not interfere with this procedure so it will be suitable for use with all the Sulphite chemicals when destroying Chlorate.

See [here](#) for more info.

Manganous Sulphate-Phosphoric Acid

Manganous Sulphate in syrupy (concentrated) Phosphoric acid solution reacts with Chlorates to form the violet coloured Mangani-Phosphate ion:



Persulphates, nitrates, bromates, iodates and also periodates react similarly.

A drop of the test solution is put into a micro crucible and a drop of the reagent is added. Warm rapidly over a micro burner and allow to cool. A violet coloration appears. Very pale colorations may be intensified by adding a drop of 1% alcoholic diphenylcarbazide solution when a deep violet colour, due to an oxidation product of the diphenylcarbazide, is obtained.

Sensitivity: 0.05 ug (micro grams). ClO_3^- .

Concentration: 1 in 1,000,000.

The reagent is made up by adding equal volumes of concentrated phosphoric acid and saturated manganese (II) sulphate solution.

Inorganic Spot Tests. F. Feigl. (Rec. Trav. chim. Pays-Bas, 1939, 58, 471-480.)

Rapid test using Ammonium Thiocyanate

See [here](#) for a rapid test using Ammonium Thiocyanate soaked test paper (pdf file).

Concentrated acids

A crude test for the presence of Chlorate can be made by placing a drop of concentrated Sulphuric acid onto a very small amount of the test sample. The test sample is made by mixing the solid that may contain the Chlorate with a similar amount of Sucrose. Grind both up to a fine powder (separately) and then mix. A drop of conc. Sulphuric acid will cause the mixture to ignite if it contains some Chlorate. It is a relatively crude test.

Pyridine

See [here](#) for a method of detection and approximate colorimetric estimation of Chlorate.

For titrations for Chlorate in cells and samples see [here](#).

Chlorides

Chlorides can be easily tested for by using a solution of Silver Nitrate. Silver Chlorate and Silver Perchlorate are soluble so they will not interfere. The test is extremely sensitive.

A drop of the Silver Nitrate solution is placed into a sample of the solution to be tested and a visible white precipitate of insoluble Silver Chloride is formed if Chlorides are present.

Hypochlorites

Starch-Iodide paper

This can be purchased from lab supply house and is cheap. Dip a strip of KI-starch paper into the solution and if the paper does not turn immediately blueish/blackish, hypochlorites are absent. If there are a lot of hypochlorites present the starch paper will not turn blue immediately but will be bleached by the hypochlorite. Take the paper out of the solution and hold it for a while and the paper at the solution edge (where it was wetted to) will turn blue after about 20 seconds if there are hypochlorites present.

Hypochlorites can be hard to eliminate completely by boiling the solution. Hypochlorites can be destroyed by adding urea or formate to the solution, about 1g/l is usually sufficient, and heating a bit.

Chlorites

If hypochlorites are absent, add about 2ml of 0.1 N sulfuric acid to about 20ml of your solution and dip the KI-starch paper into it. If it does not turn immediately blue, chlorites are absent