

# Analysis of products

When preparing chemicals for pyrotechnics compositions at home, it is important to confirm the identity and purity of the products. When impure chemicals are used the risk of accidents is greatly increased. Especially in the preparation of chlorates and perchlorates the risk is severe. The properties of each chemical in pyrotechnic compositions are very different, and very sensitive or unstable compositions may result from mistaking chlorate for perchlorates, or of not appreciating the risk of chlorate contamination sufficiently. Therefore, the identity and purity of the products should be determined. Also, in the process of preparing chlorates it is often useful to know the chloride content of a solution. Several methods that may be used to determine the composition of chloride/chlorate/perchlorate mixtures are described on this page. It will be assumed that the reader is familiar with common analytical chemistry techniques, such as pipetteing and titrating. These can be found in many textbooks.

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## Qualitative test for chlorate

Very often it is convenient to determine whether a chlorate is present in a mixture or chemical. The possibility of chlorate contamination of homemade perchlorate is inherent to the process, and a test for the presence of chlorate is then essential. Two methods to determine the presence of chlorate will be described. The first, a colorimetric test, is very sensitive, quick and simple. Unfortunately it requires the use of a chemical that can probably only be obtained from chemical suppliers. The second test is very insensitive. It will only indicate a potassium chlorate contamination worse than 20% by mass of potassium perchlorate. It may be used to distinguish between chlorate and perchlorate, but not to determine whether your homemade perchlorate is pure enough to be handled as pure perchlorate.

### Colorimetric test for chlorate

This test will indicate the presence of very slight chlorate contamination. It is convenient for testing pyrotechnic mixtures since nitrate, chloride, nor perchlorate will disturb the test.

1. Take approximately 100 mg of phenylanthranilic acid, and put this in a test tube.
2. Add 0.5 ml of concentrated sulphuric acid and shake to dissolve the phenylanthranilic

acid. This usually takes a few minutes.

3. Place a 500 mg sample of the material to be tested in a test tube and add 2 ml of water. Shake well to dissolve all chlorate possibly present. Filter if insoluble purities are present.

4. To this sample solution, add a few drops of the phenylanthranilic acid solution. An orange or red color indicates presence of chlorate. A solution of pure perchlorate or chloride merely gives a white precipitate.

#### 'Acid sensitivity' test for chlorate

This test is very insensitive but may be used to distinguish chlorate from perchlorate or indicate very heavy contamination of a perchlorate with chlorate. It relies on the fact that chlorate/sugar mixtures ignite when they contact sulfuric acid.

1. Take some sample material and make this into a fine powder with a mortar and pestle.

2. Clean the mortar and pestle well with hot water, dry it well, and then grind up some common table sugar.

3. Take 500 mg of the powdered sample and 500 mg of the powdered sugar. Mix these carefully using the [diapering method](#)

4. Place this mixture on a tile outside and drop a drop of concentrated sulphuric acid on it. If the mixture contains more than 20% chlorate it will ignite.

#### Qualitative test for chloride

When in the process of purifying chlorates, it is quite useful to determine whether the chlorate has been successfully separated from chlorides or not. Though chloride contamination is usually not very dangerous for pyrotechnic purposes, it will disturb flame colors and increase hygroscopicity of a mixture. The following test will indicate chloride contamination.

1. Take 100 mg of sample material and add 2 ml of water. Shake to dissolve any chloride possibly present. If necessary, filter to remove insoluble impurities.

2. Add a few drops of 10% (w/v) silver nitrate solution. If chloride is present, a white precipitate will form.

#### Titration to determine chloride content

When using the electrolytic procedure to prepare chlorates, this method may be used to determine the amount of chloride still present in the electrolyte. It requires some tools and chemicals not every amateur Pyro will have. It is probably not possible to do this accurately using improvised equipment.

1. First, prepare a silver nitrate solution. Dry some finely powdered analytical grade silver nitrate at 120 deg C for 2 hours and allow it to cool in a covered vessel in a desiccator. Accurately weigh about 8.5 g, dissolve it in water and make up to 500 ml in a graduated flask. Calculate the molarity from the weight of silver nitrate employed. If 'pure recrystallized' silver nitrate is used instead of analytical grade, the solution should be standardized against sodium chloride before use, using the procedure outline below. Solutions of silver nitrate should be protected from light and are best stored in amber-colored glass bottles.
2. Then, prepare an indicator solution by dissolving 5g potassium dichromate in 100 ml of water. Alternatively, and preferably, dissolve 4.2g potassium chromate and 0.7g potassium dichromate in 100 ml of water.
3. Pipette a sample of such volume as contains approximately 0.025 moles of chloride into a 250 ml conical flask resting on a sheet of white paper. Dilute to approximately 25 ml.
4. Add 1 ml indicator solution (preferably with a pipette).
5. Now, slowly add silver nitrate solution from a burette, swirling the flask constantly until the red color formed by the addition of each drop begins to disappear more slowly: This is an indication that most of the chloride has been precipitated.
6. Continue the addition drop wise until a faint but distinct change in color occurs. this **faint** reddish-brown color should persist after brisk shaking.
7. Determine the indicator blank correction by adding 1 ml of the indicator solution to a volume of water equal to the final volume in the titration and then 0.01M silver nitrate solution until the color of the blank matches that of the solution titrated. The indicator blank correction, which should not amount to more than 0.03 - 0.10 ml of silver nitrate, is deducted from the volume of silver nitrate used in the titration.
8. Repeat the titration two more times and average the results. The titrations should agree within 0.1 ml.

### **Titration to determine chlorate content**

Trace amounts cannot be detected with this method, but it is very convenient to determine the chlorate content of the electrolyte in chlorate or perchlorate cells during operation. Two procedures are described below. Both work well. The sample solution must be free of hypochlorite. This can be accomplished by reducing the hypochlorite by addition of an excess of oxalic acid, followed by titration with potassium permanganate in the usual manner.

#### **Iodometrically**

1. Treat the sample to remove hypochlorite, and dilute it such as to obtain a solution containing approximately 0.02M of chlorate.
2. Place 25 ml of the chlorate solution in a glass-stoppered conical flask and add 3 ml of concentrated hydrochloric acid followed by two portions of about 0.3g each of pure sodium hydrogencarbonate to remove air.
3. Add immediately about 1.0 g of iodate-free potassium iodide and 22 ml of concentrated hydrochloric acid.
4. Stopper the flask, shake the contents, and allow it to stand for 5-10 minutes. Iodine is liberated according to the following reaction:  

$$\text{ClO}_3^- + 6\text{I}^- + 6\text{H}^+ \longrightarrow \text{Cl}^- + 3\text{I}_2 + 3\text{H}_2\text{O}$$
4. Titrate the solution with standard 0.1M thiosulphate in the usual manner.

#### Using ferrous sulphate

1. Treat the sample to remove hypochlorite, and dilute it such as to obtain a solution containing approximately 0.02M of chlorate.
2. Place 25.0 ml of the sample solution in a 250 ml conical flask.
3. Add 25.0 ml of 0.2M ammonium iron(II)sulphate solution (Mohr's salt) in 2M sulphuric acid.
4. Cautiously add 12 ml of concentrated sulphuric acid.
5. Heat the mixture to boiling, and cool to room temperature by placing the flask in running tap water.
6. Now, either titrate the excess of  $\text{Fe}^{2+}$  with potassium permanganate or with 0.02M potassium dichromate with an indicator of 20 ml 1:1 water/phosphoric(V) acid and 0.5 ml sodium diphenyl-amine-sulphonate.

#### Gravimetric determination of chlorate

Trace amounts cannot be detected with this method, but it is very convenient to determine the chlorate content of the electrolyte in chlorate or perchlorate cells during operation. Burettes are not required, nor are carefully prepared standardized solutions. An accurate scale is however.

1. Boil the sample for 15 minutes to destroy remaining hypochlorite.
2. Dilute the sample to obtain about 100 ml of a solution containing approximately 0.2g  $\text{ClO}_3$ .

3. Add 50 ml of a 10 per cent solution of crystallized iron(II)sulphate, heat with constant stirring to the boiling point and boil for 15 minutes.
4. Allow to cool, add nitric acid until the precipitated basic iron(III) salt is dissolved, precipitate the chloride by means of silver nitrate solution, and collect and weigh as AgCl after the usual treatment.

### **Rough gravimetric determination of oxygen content**

This is a quick and simple method to determine the amount of oxygen present in a mixture of chlorides, chlorates and perchlorates. Mixtures of chlorides with chlorates or of chlorates with perchlorates are most commonly encountered. Of these mixtures, the ratio between the two compounds can be determined. It can be useful to analyze a cell electrolyte. An accurate scale is required for this method to work well.

1. Accurately weigh a test tube, and record the weight. This is  $M_1$ .
2. Place approximately 1 gram of finely powdered sample in the test tube.
3. Very gently heat the test tube at low heat to dry the sample. At regular intervals, weigh. If the weight no longer decreases the sample is dry.
4. Add approximately 100 mg of dry manganese dioxide, mix well, and weigh. Record the weight, this is  $M_2$ .
5. Now, strongly heat the sample. It will melt and decompose. After some time it will solidify. Then, heat more strongly. If perchlorates are present another decomposition reaction will take place just before red heat. Do not heat so strongly as to melt the glass tube. The decomposition will be complete before that.
6. Allow the tube to cool and record the weight. This is  $M_3$ .
7. The composition of the sample can be indicated by the formula  $KClO_x$ ,  $x$  being the molar oxygen content. So, for chlorides  $x = 0$ , for chlorates  $x = 3$  and for perchlorates  $x = 4$ . Values in between are mixtures (eg  $x = 3.5$  indicates a 50:50 mixture of chlorate and perchlorate).

X can now be calculated using the following formula:

$$x = \frac{(M_3 - M_2) * M_y}{16 * (M_3 - M_1)}$$

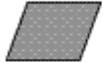
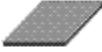
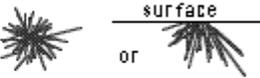
Where  $M_y$  is the molar mass of the chloride. For example, if the sample consisted of potassium salts,  $M_y$  is the molar mass of potassium chloride, 74.6g.

### **Crystal shapes**

Another quick (but unreliable) way to distinguish between chlorates and perchlorates is by observing the crystals that form upon recrystallization. This is not a reliable method and only works if there is either a large fraction of chlorate in the mixture or if you know for sure you have either pure chlorate or perchlorate. In the latter case this can be used as a simple and reasonably reliable test to distinguish between the two compounds. The crystals shapes described below are valid only for potassium compounds and not for sodium or ammonium compounds.

### Possible shapes

Crystals that form from  $\text{KCl}/\text{KClO}_3/\text{KClO}_4/\text{NaCl}/\text{NaClO}_3/\text{NaClO}_4/\text{HCl}$  mixtures in various compositions come in many different shapes. The most common shapes seen are these:

through a microscope	By the bare eye	crystal shape
		monoclinic
		monoclinic
		rhombic
		rhombic

The first crystal type, 'flat plates', is potassium chlorate,  $\text{KClO}_3$ . The crystals that form are very thin plates, almost square. They sometimes refract light in many colors since they are so thin initially (of the same order of magnitude as the wavelength of light). They are quite light and float in the solution and on its surface. When they grow larger they sink and stop refracting colored light.

The second crystal shape, sometimes described as 'cactus needles', is also potassium chlorate,  $\text{KClO}_3$ . It looks entirely different from the first shape, but the lattice structure is the same. The crystal shape is influenced by the presence of other species in the solution from which it crystallizes (such as remaining unconverted chloride).

The third crystal shape is impure potassium perchlorate,  $\text{KClO}_4$ . It looks like needles, but the way they grow together is different from the cactus needles. They don't form clusters like the cactus needles and grow longer and thinner. Under a microscope you can clearly

see they are rhombic. Pure potassium perchlorate looks different, and the difference is again caused by presence of impurities.

The fourth crystal shape is pure potassium perchlorate,  $\text{KClO}_4$ . When you crystallize a solution slowly enough fairly large crystals can form from the solution (up to 0.5 cm or so). These are clearly rhombic as can be seen with the bare eye. Under a microscope smaller crystals can be identified quite easily.

These conclusions were drawn after crystallizing from solutions of every possible combination of the compounds mentioned above and are confirmed by powder X-ray diffraction analysis.