# THE CHLORINE PRODUCTIVITY OF MIXTURES OF POTASSIUM CHLORATE AND TINCTURE OF FERRIC CHLORIDE.*

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Prescriptions which call for the mixing of potassium chlorate and tincture of ferric chloride are quite common. Usually with these ingredients there is prescribed glycerin, simple or flavored syrup, elixir or other alcoholic or aqueous diluent, and alum, potassium citrate and other additions may be ordered.

Some pharmacists are of the belief that the doctor expects chlorine to be produced and dispensed in all such mixtures. Others hold the opinion that no chlorine is wanted, and besides, that none will be present in the finished prescription, unless the potassium chlorate and tincture of ferric chloride are heated together before being diluted to finish the prescription. Still others have remarked on the relatively small amount of chlorine that is noted even when the last-named treatment is applied to the mixed chlorate and tincture.

Besides the mentioned additions to these prescriptions, diluted or full strength hydrochloric acid may be ordered as an ingredient.

The effect of different dilutions of hydrochloric acid on potassium chlorate will be dealt with in the course of this paper.

Any production of chlorine upon mixing just the potassium chlorate and tincture of ferric chloride will, of course, be due to the free acid contained in the tincture, which acid is derived from the solution of ferric chloride from which the tincture is prepared; for, as is well known, to keep these preparations clear by avoiding the formation of ferric oxychloride, the Pharmacopœia allows both of them to have an acid reaction. The ferric chloride as such does not enter into the reaction which liberates the chlorine.

The simplest expression of change that can be fancied as taking place between potassium chlorate and hydrochloric acid to give chlorine would be as follows:

$$KClO_3 + 6HCl = KCl + 6Cl + 3H_2O$$

But when potassium chlorate and hydrochloric acid actually react there is produced a yellowish gas known as "euchlorine," which is regarded as a mixture of free chlorine and chlorine dioxide; and its production is usually explained by the equation:

$$4KClO_3 + 12HCl = 4KCl + 6H_2O + 3ClO_2 + Cl_2$$

Whether one or the other of these equations is accepted, the chlorine potentiality is seen to be dependent upon the actual acidity, and consequently the amount of chlorine that can be produced depends upon the quantity of absolute hydrochloric acid in the materials which are mixed; for the chlorine of the chlorate is not available, but, as shown by the equations, remains combined with the potassium.

Again, if it is the pharmacist's intention to obtain as much as possible of any chlorine that may be liberated when the chlorate and tincture are brought together, the mixing will likely be done in an entirely dry bottle that is stoppered soon after

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the introduction of the second ingredient; for experience has shown that if only a few drops of strong hydrochloric acid are put into a bottle that has just been rinsed, there may be but little or no generation of chlorine.

The N. F. V formula for **Liquor Chlori Compositus** will give some idea of the proportions of potassium chlorate and hydrochloric acid required, as also of the handling and diluting of these materials to produce a solution of sufficient chlorine strength to be recognized as of value. This solution shows 0.35% chlorine.

To determine what one is likely to get as chlorine or its compounds of like color, odor and effects, when potassium chlorate and tincture of ferric chloride are mixed, the following prescription was taken to three of Philadelphia's well-known dispensing pharmacies:

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|---|---|
| Potass. Chlorate | 2 drs. |
| Tinct. Chloride Iron | 2 drs. |
| Glycerin | 2 drs. |
| Simple Syrup | 4 drs. |
| Water enough to make | 2 ozs. |
| Mix | |
| Label—dilute with water for use as gargle. | |

There was also obtained from each store a specimen of its tincture of ferric chloride.

The question to be settled is—"Do these finished prescriptions contain free chlorine, and, if so, how much?"

There is no more delicate test for free chlorine than the starch and iodine test which occurs through the liberation of iodine when chlorine is brought into contact with potassium iodide; but, due to the fact that ferric salts themselves liberate iodine from potassium iodide, it was necessary to avoid contact of the tincture and the potassium iodide; and this was done by drawing any chlorine that was produced by the reacting materials out of the container in which the mixtures were made and into the potassium iodide solution.

For this purpose an aspirating apparatus was constructed as follows: an Erlenmeyer flask was provided with a tube to lead the air through a strong solution of potassium hydroxide (to absorb atmospheric chlorine) and with another tube leading into a flask filled with absorbent cotton (to trap any droplets of alkali which might be carried forward by the air current). This second flask was in turn connected with a third flask (the reacting flask) in which the materials to be examined were placed. It was connected with a side-tube fractionating flask by leading a tube through mouth of same to bottom, using side tube as escape, so as to trap alcohol, water or other liquid which might be carried forward. To the side tube of this fourth flask there was connected another Erlenmeyer flask in which was put a solution of potassium iodide mixed with starch paste (test flask), and from this fifth flask a rubber tube led to a suction pump.

All of the experiments recorded herein were made in this apparatus; each time before the apparatus was used for another experiment it was thoroughly cleansed and tested for several minutes by drawing air through it to prove the absence of chlorine.

This apparatus ready, each of the three prescriptions was examined within eight hours of the time that it was compounded.

The bottle containing the prescription, unopened until now, was well shaken and one fluidounce poured into the reacting flask, all connections having previously been shown to be tight, and suction applied.

Air drawn through the cold prescriptions for five minutes showed no effect on the test flask, thus proving the absence of chlorine gas. When, however, the reacting flask was placed in boiling water, the test flask soon showed the presence of chlorine, but only in very small amount as indicated by the fact that the contents of the test flask, upon prolonged application of heat, required only 0.15 cc., 0.1 cc. and 0.1 cc. of $N/10$ $Na_2S_2O_3$ (Sodium Thiosulphate) to discharge the blue color produced by the iodine and starch, for the three prescriptions in the order in whch they were handled.

When it is remembered that 1 cc. of $N/10$ $Na_2S_2O_3$ is the equivalent of 0.003546 Gm. of Cl, the very minute amount of chlorine possible of production by heating the finished prescription will be appreciated.

These quantities figured into percentage of prescription would be 0.00177%, 0.00118% and 0.00118%.

Some further idea of this amount of chlorine may be gathered by noting that the National Formulary states for its chlorine water a strength of 0.35 Gm. of chlorine in 100 cc. of the product, or 0.35%; which makes these prescriptions capable of yielding but $^1/_{300}$ to $^1/_{200}$ of the chlorine strength of the N. F. V chlorine water, when so treated.

Next there arises the question whether, on standing, such prescriptions develop chlorine. To learn about these, 11 days after they had been compounded and examined as above outlined, the other half or one fluidounce of each of the three prescriptions (which during this time had remained in the securely stoppered bottle) was well shaken and placed in the reacting flask of the apparatus. Five minutes' aspiration in the cold showed no chlorine in any of these prescriptions; but upon the application of boiling water to the reacting flask there was obtained exactly the same amount of chlorine as the freshly compounded prescription had shown.

These results show conclusively that there is no chlorine generated in such mixtures when made without heat, either at once or upon reasonable standing.

In order to learn what happens in the way of liberation of chlorine when potassium chlorate and tincture of ferric chloride are mixed, several experiments were made using 1 drachm of potassium chlorate and 1 fluiddrachm of the tinctures of ferric chloride purchased at the stores where the prescriptions had been compounded.

No chlorine was found to result from the mixing of chlorate with these three lots of the tincture, until the reacting flask was set in the boiling water, when chlorine was promptly developed by all of them and in abundance.

By prolonging the application of heat through immersion in boiling water until chlorine was no longer produced, and drawing all of it over into the potassium iodide solution, the three lots of the tincture yielded chlorine in equivalence of $N/10$ $Na_2S_2O_3$ as follows: No. 1, 49.3 cc.; No. 2, 50.8 cc.; No. 3, 47.8 cc. or 329, 508 and 478 times as much as was produced in a portion of the corresponding prescription equivalent to the fluiddrachm of tincture used.

All of these results taken together plainly show that the three pharmacies

from which the prescriptions were purchased make no special effort to see that the mixture generates chlorine. The results also show that the degree of dilution of the active acidity as well as its total amount is a factor to be reckoned with in mixing potassium chlorate and tincture of ferric chloride when the production of chlorine is intended.

In these experiments with the potassium chlorate and the tincture, by the time the liberation of chlorine had been completed, the contents of the reacting flask were found to have dried to a powder. These powders were not completely soluble in water, hot or cold, because of the formation of iron oxychloride or of hydrated oxide of iron, a condition which indicated the complete or nearly complete consumption of all free hydrochloric acid. However, the soluble portions imparted strong acidity to their water solutions, and when the turbid liquids were filtered, solutions colored golden-yellow by the ferric chloride were obtained.

It having been found that chlorine can be generated in the bottle by heating the mixture of potassium chlorate and tincture of ferric chloride by immersion in hot water, it was decided to learn whether the relative size of the bottle would make a difference in the amount of chlorine that will be liberated in the container and thereafter taken into solution by the liquid to be used for the dilution of the prescription in adjusting its final volume.

Accordingly, three lots (corresponding to the prescription) of a mixture of 2 drachms of chlorate and 2 fluiddrachms of tincture were placed in dry 2-ounce, 4-ounce and 8-ounce bottles which were provided with sound corks. These bottles were placed in a vessel of water and this brought to boiling while the stoppers were held in the mouths of the bottles by covering them with the hand. Finally, because of pressure of alcohol vapor in the bottle more than of any pressure of chlorine gas, the stoppers were ready to "blow," and some did. But unblown representative bottles were taken from the hot bath and to their contents cold water was added in portions of about four fluiddrachms at a time, with vigorous shaking, the bottle being kept stoppered between additions of water.

The contents of each bottle were brought to two fluidounces, and the resulting mixtures were examined for chlorine by placing one fluidounce in the reacting flask and drawing the chlorine into the test flask as usual.

The results were close to the following figures in $N/10$ $Na_2S_2O_3$: from the 2-ounce bottle, 0.19 cc.; from 4-ounce bottle, 0.27 cc. and from 8-ounce bottle, 0.5 cc. All of these mixtures had distinct odors of chlorine.

When the same quantities of chlorate and tincture were mixed cold and diluted to the same volume (two fluidounces) and one fluidounce of it then heated in boiling water (with less danger), they showed a production of chlorine equivalent to 0.15 cc. $N/10$ $Na_2S_2O_3$; which approximated the amount of chlorine obtained in a 2-ounce bottle by the more dangerous method of heating the chlorate and tincture before dilution.

It is very evident that there is opportunity for loss of considerable chlorine when the chlorate and tincture mixture, after heating, is being diluted with water, as the chlorine gas easily passes out of the bottle as the water is put into the container. It is also interesting to note that the N. F. V exacts but about one-half of the chlorine theoretically obtainable from the hydrochloric acid used in the preparation of **Liquor Chlori Compositus.**

To check up on the materials used, continued aspiration of air made through several specimens of tincture of ferric chloride with or without heat did not lead to liberation of iodine in the test flask, a result that clearly shows the absence of chlorine or similarly reacting gases in the tincture.

When cold official hydrochloric acid (31–33%) was treated in the same way it did not color the test liquid, but when placed in boiling water it brought about a slight purplish tint in the test flask.

Next, to determine the approximate strength of the weakest dilution of hydrochloric acid which will react with potassium chlorate at room temperature with liberation of gas that passed into potassium iodide solution will give a blue color with starch, a series of dilutions of official hydrochloric acid were made as follows: 10%, 5%, 2.5%, 1%, 0.5%, 0.375%, 0.25%, 0.1% and 0.01% of actual HCl.

These dilutions were tried with powdered potassium chlorate in the proportion of one drachm of the chlorate and one fluiddrachm of the diluted acid.

The three weakest dilutions showed no reaction with the chlorate either in the cold or when heat was applied to the reacting flask as described.

The next three dilutions 0.375%, 0.5% and 1% showed no effect in the cold, but when the reacting flask was set in boiling water all promptly showed a steady liberation of chlorine, and the stronger the acid the quicker this effect was seen.

Further experimentation showed that 2.5% hydrochloric acid is about the weakest dilution of this acid that will generate chlorine from potassium chlorate at room temperature; and although there was distinct odor of chlorine in the reacting flask but little color of the gas was observable as resulting from the use of acid of this strength.

When 5% hydrochloric acid was added to the chlorate, chlorine was immediately generated as shown by the test flask, and upon application of hot water to reacting flask, both it and the trap flask beyond showed plenty of the yellowish green gas.

A 10% hydrochloric acid, which is the official diluted acid, instantly liberated enough chlorine to show in the test flask, although but little color was noted in the reacting flask until the boiling water-bath was applied, when the reacting and next flask showed an abundance of chlorine gas. The N. F. directs hydrochloric acid diluted with an equal volume of water (equivalent to about 15% acid) for action on the chlorate with aid of water-bath temperature in making of **Liquor Chlori Compositus.**

Results thus far having indicated that the production of chlorine depends upon the amount of hydrochloric acid present and the degree of its concentration, it was decided to try a mixture of one drachm of potassium chlorate and 0.35 fluid drachm of the official solution of iron chloride, or the amount of this solution contained in one fluiddrachm of the tincture.

This mixture gave chlorine at once in the cold (showing an acidity equal to at least 2.5% of absolute hydrochloric acid) and on continued subjection to the heat of boiling water showed a total chlorine production that checked closely with the amounts produced by the one-drachm lots of the several tinctures.

When tincture of ferric chloride was replaced with the N. F. Tincture of Citrochloride of Iron which has the same ferric chloride content (but in which the free acid is neutralized by treatment with an excess of sodium citrate, with consequent

liberation of citric acid) there was no chlorine developed either in the cold or upon application of heat.

Nor did a mixture of one drachm of potassium chlorate and two drachms of citric acid in the presence of two fluiddrachms of water show any liberation of chlorine in the cold, and but a very slight discoloration of the test flask on prolonged heating of the reacting flask (perhaps due to trace of mineral acid in the citric acid).

Tartaric acid acted in the same way, likely for the same reason.

When a mixture of one drachm potassium chlorate and four drachms of powdered alum and two fluiddrachms of water were treated no chlorine was generated either in cold or by heat.

A mixture of one drachm of potassium chlorate and two fluiddrachms of U. S. P. Acetic Acid (36%) did not generate chlorine under either temperature.

The presence of glycerin seemed to make no difference with the reaction of the chlorate and tincture in the cold; but when the application of boiling water was continued until the alcohol of the tincture had distilled over, a violent reaction occurred in the reacting flask, the contents taking fire and developing back pressure. But fortunately no such reaction is likely to be encountered in the ordinary compounding of this prescription.

A mixture of sodium chlorate one drachm and one fluiddrachm of tincture of ferric chloride promptly showed development of chlorine in cold equivalent to 0.1 cc. of $N/10$ $Na_2S_2O_3$, and upon the application of heat about the same amount was shown with this tincture and potassium chlorate.

Hydrochloric acid of 2.5% strength acid was also found to be the weakest dilution that decomposed sodium chlorate in the cold.

## CONCLUSIONS.

The mixing of potassium chlorate and tincture of ferric chloride without application of heat does not produce chlorine, either at once or upon standing.

The momentary heating together of these ingredients, as for instance in the bottle in which the prescription is to be dispensed, produces some chlorine, the stated amounts yielding perhaps a maximum of one-sixtieth to one-fortieth of the 0.35% of chlorine contained in the chlorine water of the N. F. V.

Regardless of what the prescriber may intend, it will be seen that but little chlorine can be produced, unless the chlorate is first acted upon by a sufficiently strong hydrochloric acid.

Should a physician express himself as expecting chlorine to be dispensed in mixtures of potassium chlorate and tincture ferric chloride, attention may be directed to the fact that but little of it is actually procurable from these ingredients; and that, to provide chlorine in amount comparable to the strength of the N. F. V chlorine water, hydrochloric acid must be included as an ingredient.

The proportions of chlorate and acid prescribed by the N. F. V for its chlorine water will serve as a guide when such considerable amounts of chlorine are wanted.

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