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REPORT
of
COMMITTEE ON EXAMINATION

This is to certify that we the undersigned, as a Committee of the Graduate School, have given Floyd Edward Joyce final oral examination for the degree of Master of Science. We recommend that the degree of Master of Science be conferred upon the candidate.

Minneapolis, Minnesota

June 6, 1917.

J. H. Hunter.
Chairman

C. J. P. Pettibone

E. S. Brown

REPORT
of
COMMITTEE ON THESIS

The undersigned, acting as a Committee of the Graduate School, have read the accompanying thesis submitted by Floyd Edward Joyce for the degree of Master of Science. They approve it as a thesis meeting the requirements of the Graduate School of the University of Minnesota, and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science.

Minneapolis, Minnesota

June 6, 1917

J. H. Hunter
Chairman
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Thermal Decomposition of Silver Salts of
Phenols Containing More
Than One Kind of
Halogen

A Thesis
Submitted to the
Faculty of the Graduate School
of the
University of Minnesota

by
Floyd E. Joyce

In partial fulfillment of the requirements
for the degree of
Master of Science

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MOM
585

THEORETICAL PART

An earlier work by Torrey and Hunter¹ attempted to account for the two chromo-isomeric forms of 2,4,6 tri-brom phenol. During the progress of this work it was found that the red silver salt of this phenol on treatment with ethyl iodide darkened, turned green and gradually turned to a blue color. Following the production of the blue color the solution began to fade and change to a yellowish-brown. After standing ten minutes the mixture was filtered and to the filtrate 95 o/o alcohol was added. This caused a precipitation of a white powdery material whose composition was unknown.

Later work by Hunter, Daniels et al² showed that this peculiar reaction is obtained by boiling benzene and by the action of heat alone. Experiments were tried by these authors on trichlorophenol and tribromo resorcinol monomethyl ether to determine whether a similar reaction would result. With benzene the silver salt of tri chloro phenol reacted without color changes giving a solid gray in color. The clear solution on precipitation with gasoline yielded a white amorphous substance similar to the one from tri-bromo-phenol. The same silver salt yielded with ethyl iodide the phenetol and a very small amount of material precipitated by alcohol. With tri bromo-resorcinol monomethyl ether and hot benzene a blue color was obtained which disappeared later and from the solution a copious precipitate of the amorphous compound was obtained. As in the case of tri chloro phenol a small yield of the amorphous compound resulted on treatment with ethyl iodide. Woollett³ obtained similar results

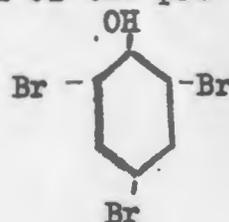
¹J. Am. Chem. Soc., 33, 194 (1911) cf. Hantzsch, B. 40, 4332 (1907)

²J. Am. Chem. Soc., 37, 1761 (1916)

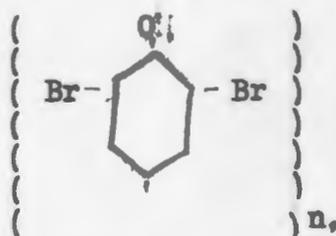
³J. Am. Chem. Soc., 37, 2474 (1916)

with the silver salt of tri-iodo phenol.

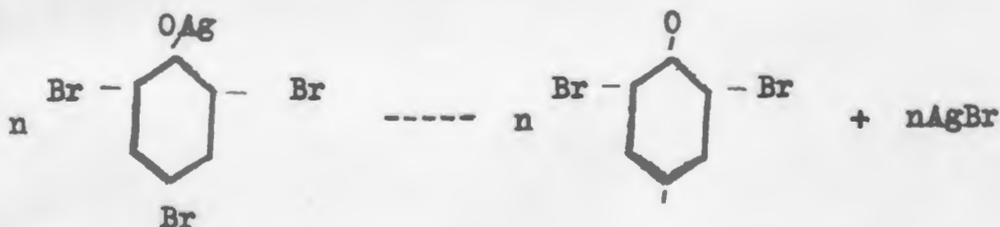
The evidence seems to show that all silver salts of tri-halogenated phenols decompose catalytically in the same manner and with the production of the unknown amorphous substance. The work of Hunter, Daniels and Olson¹ showed that the composition of the precipitate from the decomposition of the silver salt of



is that indicated by the formula



an unsaturated residue being formed from the catalytic decomposition of the salt which polymerized to an amorphous compound of high molecular weight. It is evident then that one atom of halogen is split out as indicated by the equation:

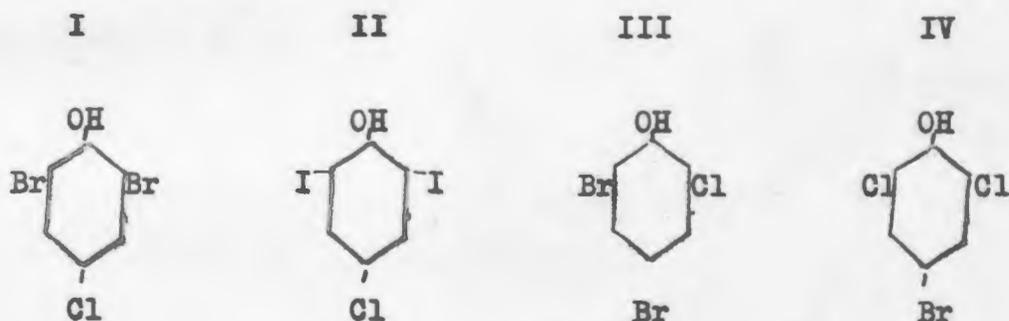


The problem presented in our work is a double one; first, in a salt of a symmetrically halogenated phenol, is the halogen atom with which the silver splits out in the ortho position or in the para position? Second, if two kinds of halogens are present, which kind will be preferred by the silver? It is obvious that in any given phenol with two different halogens both of these factors will be

¹Loc. cit.

operating at the same time. If there is a difference in the effect of position or of kind of halogen, comparative data, for instance, on phenols containing (a) two chlorine atoms in the ortho position and a bromine atom in the para (b) two bromine atoms in the ortho position and a chlorine atom in the para position, should bear out this point. This will be given presently.

For the practical consideration of the problem the following phenols were prepared:



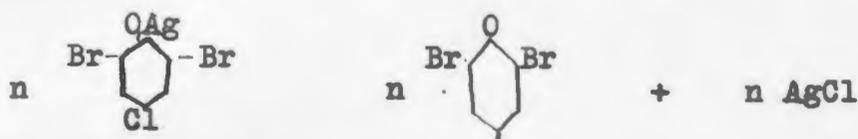
The plan of the work was to prepare the silver salts of these halogenated phenols and decompose them with boiling benzene. This is a thermal decomposition, but it was shown by the earlier work that the decomposition in this case took the same course as the catalytic action with ethyl iodide. Then after filtering off the silver halides split out during the decomposition the benzene solution was treated with alcohol to precipitate the amorphous compound. The amorphous compound was then analyzed by the method of Carius for halogen. This method does not include a separation of mixed halogens, so four well known methods were compared for finding the percentages of the individual halogens could be estimated. The first plan was to convert, in a mixture of silver bromide and silver chloride, all of the bromide into silver chloride by direct chlorin-

ation. No satisfactory results were obtained, however, as the silver bromide was incompletely changed to the chloride as shown by several determinations. The next method was based on the solvent action of sodium thiosulphate on silver halides. After solution of the mixed halides the silver was precipitated with sodium sulphide as the sulphide and from the amount of silver found the halogens calculated indirectly. Here again the results obtained were far from satisfactory, the difficulty being due to an incomplete precipitation of the silver. The third method was tried for the mixed silver halides of iodine and chlorine. Separation of these two was affected very satisfactorily by treatment with 3 o/o ammonia which dissolves the silver chloride very readily but has no action upon the iodide. It was found that ammonia stronger than this exerted a solvent action upon the iodide. So that the specific gravity of this solvent was carefully determined before attempting to separate these two halides. A fourth method consisted in treating the mixed silver chloride and silver bromide with potassium cyanide. Complete solution took place and the silver was determined electrolytically. By this indirect method the proportion of chlorine and bromine agreed very well in duplicate samples. This method then was used throughout this work where mixtures of silver chloride and silver bromide were involved.

Thus, from the quantity and kind of halogen found in the amorphous compound it is possible to determine what per cent of halogen is split out from the ortho position and what per cent from the para. Also, the relative affinity which the different halogens have for the benzene ring may be learned.

Discussion of Results

For a working hypothesis it was assumed, at the beginning of this research, that in the decomposition of the silver salts, the para atom would show the greatest tendency to split off. In the decomposition of the silver salt of para chlor 2,6 di-brom phenol, then, the change would be expected to take place in this manner.



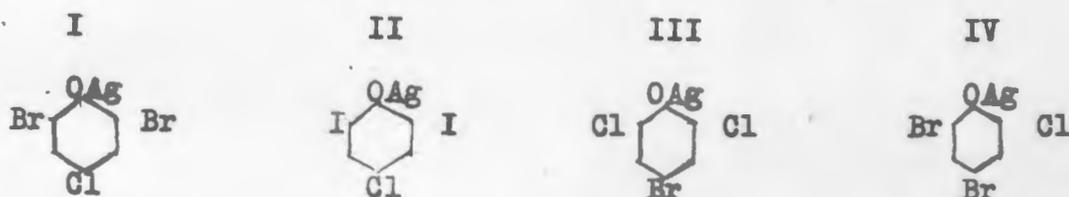
The data on the unsaturated residue formed in this reaction showed that on the average 10.24 o/o of chlorine was present and 49.14 o/o of bromine in the amorphous oxide resulting. If the para position was the only one attacked a complete removal of the chlorine would take place. But, if the ortho position was attacked none of the chlorine could be removed and only bromine would come out. From the formula $\text{C}_6\text{H}_2\text{ClBrO}$ there should be 17.27 o/o chlorine in the molecule if one of the halogens in the ortho was removed. This is the maximum amount of chlorine available. The results show 10.24 o/o remained in the amorphous oxide.

This 10.24 o/o is 59.24 o/o of the available chlorine. Therefore, 59.24 o/o of the molecules of silver salt decomposed in such a way as to retain the chlorine atom. In other words, the silver split out with one of the bromines in the ortho position. Hence we see that in the sample in question, 59.24 o/o of the molecules split out AgBr, "reacting ortho", and 40.76 o/o split out AgCl, "reacting para." Here, contrary to expectation, more of the molecules "reacted ortho" than para.

A factor to be considered at this point is the relative activi-

ty of chlorine and bromine. Complete removal of the chlorine could not be expected if chlorine shows greater affinity for the nucleus than for the silver. As we have seen, our original hypothesis in regard to the para position does not hold. Either the chlorine has too great affinity for the ring or the tendency is for the ortho atom to split off, rather than the para. These factors acting together tend to distribute the pulling power of the silver so that its action is greater at the weaker position.

Before more can be said on this point, the results from the other salts must be considered. Following is a table from all four salts:



Total halogen	59.38	66.70	47.86	62.41
Bromine	49.14	(I)57.64	11.95	55.07
Chlorine	10.24	9.06	35.90	7.34
o/o para	40.76	35.46	69.26	
o/o ortho	59.24	64.54	30.74	

The second of these salts, that of para chlor 2,6 di-iodo phenol, shows results similar to that of the first one. Iodine was found in the amorphous oxide to the extent of 57.64 o/o and chlorine 9.06 o/o. This percentage of chlorine, calculating from the formula C_6H_2IClO , is 64.54 o/o of the maximum amount possible and must necessarily represent the extent of the reaction in the ortho position; 35.46 o/o represents the reaction in the para. The results

from this analysis, then, seem to indicate that the general plan of the decomposition followed is the same as that of I.

The results on III, the silver salt of para brom 2,6 di-chlor phenol, differ from those obtained on I and II. Here only 11.95 o/o of bromine was found while the chlorine amounted to 35.90 o/o. Calculating as before for the theoretical amount of bromine it was found that 38.99 o/o represents the amount called for by theory. The percentage of bromine remaining in the amorphous oxide is 30.74 which represents the extent of the reaction in the ortho position, 69.26 o/o is the amount in the para. A comparison of the results on this salt with those obtained on the first salt explains the second part of our double problem. Inspection of the structural formulae shows that the position of the chlorine and bromine is interchanged. These two phenols were mentioned in the theoretical part as being the ones most likely to show the relative activity of chlorine and bromine. In salt number I chlorine occupies the para and bromine the ortho positions. Here the extent of the decomposition in the ortho position amounts to 59.24 o/o while in the para it is 40.76 o/o. On the other hand, when bromine is in the para position and chlorine occupies the ortho position, the ortho atoms react only 30.74 o/o, while the reaction para amounts to 69.26 o/o. We have seen already that the decomposition of the salts affects both positions, but that position which is occupied by the less active halogen of two splits out more readily. In this case where the halogens were interchanged we can only conclude that the weaker element is removed with greater ease.

Silver salt number IV decomposed in such a way as to give percentages of chlorine and bromine nearly like those obtained in the

amorphous oxide formed from number I. The arrangement of the halogens in this salt where the chlorine is in the 2nd position and the bromine in the 4th and 6th positions, makes it impossible to determine the extent of the reaction in the ortho and para. Both chlorine and bromine occupy ortho positions in this salt. This is particularly interesting because the work on salts I and II shows that the less active element is removed, and in this case the less active halogen had the advantage of being in both the ortho and para positions. Further work would be necessary in order to clear up this point.

As previously stated, it was assumed that in the thermal decomposition of the silver salts under examination that the para atom would split out more easily. The data derived from silver salts I and II does not show this, as we have seen, but the data from all of them shows that both positions, the ortho and para, are affected. The other part of the problem we have been considering, which of two kinds of halogens is preferred by the silver, is made clear by the reactions of salts I and III, where the position of chlorine and bromine is interchanged. In number I the decomposition was greatest at the ortho position occupied by bromine, while in number III the decomposition was greatest in the para position also held by bromine.

Addendum

The color of the silver salts.

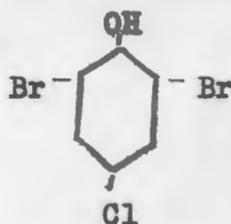
- I White
- II White
- III Yellow
- IV Orange

It is interesting to note that in the colored salts of para brom 2,6 di-chlor phenol and 2 chlor 4,6 di-brom phenol, one atom of chlorine is in the ortho position. However, the silver salt of para chlor 2,6 di-brom phenol shows a peculiar change. When first precipitated, it was orange colored but on standing, it changed to white. This tendency is no doubt due to the presence of chlorine, but just why this salt should show a change when chlorine is in the para position is not understood. It is probable that a chromo isomeric rearrangement of some kind takes place when the salt is first precipitated. As it had no bearing on the problems presented in the paper, no work along this line was undertaken.

Experimental Part

Preparation of the Phenols

I. Parachlor 2,6 di bromophenol



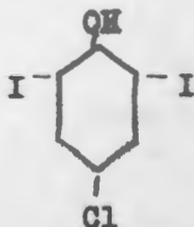
For the preparation of this phenol, which has not been described, a quantity of p-chlor phenol was redistilled giving a product melting at 43°. A weighed quantity of the phenol was dissolved in glacial acetic acid and the calculated amount of bromine added by means of a dropping funnel. After the bromine had all been added, the acetic acid solution was allowed to stand until cool and diluted with water to precipitate the newly formed phenol. The precipitate was filtered off and washed first with strong acetic acid and then will dilute acid and finally with water. The washed and dried product was recrystallized from alcohol in long shiny needles. The melting point of the p-chlor-2,6 dibromophenol was found to be 92°. An analysis of a sample gave the following results:

Sample .2995

Calculated for $C_6H_2Br_2ClOH$ 68.21 o/o

Found 68.28 o/o

II. P-chlor 2,6 diiodo-phenol



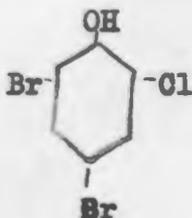
No information regarding the preparation of this phenol was available so the following method was tried. Thirty-one and seventhe grams of iodine and 13 grams of potassium iodate were dissolved in dilute potassium hydroxide. Into this 20 grams of p-chlor phenol dissolved as potassium hydroxide werepoured. The whole was placed in a two liter bottle and, with careful addition of dilute sulphuric acid, shaken vigorously until all of the iodine was precipitated. Shaking was continued then for an hour when the phenol began to precipitate and gather in small pellets. These were made up chiefly of p-chlor-2-6 di-iodo-phenol colored with iodine. Dilute potassium bisulphite was then added to remove the free iodide and the precipitate filtered off. Repeated crystallization from alcohol gave a light brown product melting at 107-8°. It was analyzed for chlorine and iodine, with the following results:

Sample .3170

Calculated for C_6HClI_2OH 76.07 o/o

Found 75.90 o/o

III. O-chlor 4,6 di brom phenol.



This phenol, first described by Garzino¹, was prepared for this research as follows: Fifty grams of ortho-chlor phenol were dissolved in an equal amount of glacial acetic acid. A 10 o/o excess of bromine, 42.6 c.c., in the same amount of glacial acetic acid

¹B. 25 (2) 111

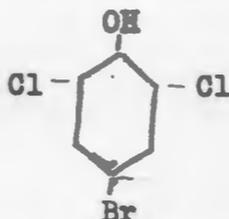
was added slowly and with vigorous stirring to the dissolved phenol. Considerable evolution of heat took place during the process of bromination. On allowing the reaction product to cool needle-like crystals separated out. These were re-crystallized repeatedly from glacial acetic acid to constant melting point, 80 degrees. A sample taken for analysis contained practically the amount of halogen called for by theory.

Sample .3612

Calculated for $C_6H_2ClBr_2OH$ 68.21

Found 68.30

IV. P-brom 2,6 dichlor phenol



Ling¹ prepared this phenol by treatment of para brom phenol with sul chloride. This method was tried but no satisfactory results were obtained, so chlorination of para brom phenol was tried. Para-brom phenol made by Hantzsch's² method was first prepared by dissolving 28.5 grams phenol in 250 c.c. of carbon bi-sulphide and to this 15 c.c. of bromine in 50 c.c. of carbon bi-sulphide were added slowly. After the bromine had all been added and the reaction mixture allowed to stand for a time, the solvent was evaporated off. The residue subjected to distillation in vacuo yielded an excellent product of para brom phenol melting at 64°. To a known amount of this phenol dissolved in glacial acetic acid

¹Soc. 61, 560
²Ber., 28, 978

the calculated amount of chlorine was added by careful weighing. The acetic acid solution when cool precipitated long glistening crystals, which were carefully washed with dilute acetic acid. They were crystallized twice from alcohol and water and the melting point taken. The result 66.5° agreed exactly with that obtained by Ling so the phenol was not analyzed.

The Silver Salts.

All of the silver salts of the phenols were made in the following manner: About 20 grams of the phenol were placed in a beaker covered with water and treated with dilute caustic potash until solution was brought about. The alkaline solution was then made barely acid with 2 o/o acetic. A slight precipitate indicated that the potassium phenolate and acetate were present in the solution which is alkaline due to hydrolysis of the phenolate. A few drops of dilute silver nitrate solution were then added to remove any free ions of chlorine or bromine. It was allowed to stand a while, and then filtered. To the filtrate 5 o/o silver nitrate was added until no further precipitation occurred. The precipitate was filtered and washed with plenty of water to remove excess of silver nitrate, transferred to a Buechner funnel to remove excess of water. After removing as much of the water as possible this way the silver salt was spread out on a watch glass and allowed to dry in the air but in the absence of light.

I. The silver salt of 2,6 di-bromo p-chlor phenol.

This salt when first precipitated was orange in color but on standing a few minutes it gradually turned white. A portion of this white precipitate, when dissolved in ammonium hydroxide and acidified, precipitated orange as before with the accompanying

change to white. The dry salt, when treated with cold ethyl iodide, turned a light green color with a suggestion of blue and finally to a darker green. With warm ethyl iodide the preceding color changes were again noted with the exception that the final dark green color did not result. Cold benzene gave no color reaction whatsoever but with hot benzene there was a formation of the blue color, which changed to yellow with an intermediate green color. For the preparation of the amorphous compound formed by this salt two grams of the dry material were boiled for twenty minutes in benzene. The precipitate was filtered off and the benzene solution treated with alcohol precipitated a yellowish-white amorphous compound. This was purified by twice dissolving in benzene and precipitating with alcohol. After drying it was ready for analysis. Yield .76 grams or 38 o/o.

Ethyl Ether of p chlor di-brom phenol.

This had not been described. It was prepared by covering a few grams of the silver salt with alcohol and then adding ethyl iodide, and allowing to stand. After filtering off the silver iodide and evaporating the filtrate, the residue consisting chiefly of the ethyl ether, was purified by crystallization from water and alcohol. Melting point 52.5°.

Analysis. Sample .0956

Calculated for $C_6H_2ClBr_2OC_2H_5$ 62.15 o/o

Found 62.07 o/o

II. The Silver Salt of 2,6 diiodo-para chlor phenol.

This salt was made as described above. It has a greenish-white color. During the precipitation no color changes were observed. The action of cold ethyl iodide on the dry salt was tried.

No change was observed but with hot ethyl iodide a vigorous reaction took place with color changes. A green color developed followed by a deep blue which turned to a green. The action of cold benzene was tried but no change occurred. In the preparation of the amorphous compound derived from this salt boiling benzene produced identically the same color changes as warm ethyl iodide.

III. The Silver Salt of O-chlor 4,6 di brom phenol.

When first precipitated it was thought that the orange color which characterized it would disappear on standing. This change did not take place so the action of very dilute ammonia was tried, but the salt retained its original color. As the color seemed stable the precipitate was dried and its action with ethyl iodide and benzene tried. With cold ethyl iodide a pale green color was observed. With hot ethyl iodide the salt swelled and green, blue, and yellow colors were observed successively. The filtrate, after removing the silver iodide, gave a white precipitate with alcohol. Six grams of the silver salt boiled with 75 c.c. benzene produced no color changes; .5 grams of amorphous material was obtained or 8 o/o.

IV. The Silver Salt of 2,6 di-chlor 4 bromo phenol.

The color of this salt is yellow, the color of the salt when first precipitated. On this compound with cold and hot ethyl iodide produce the same color changes, a green changing to a distinct blue. The filtrate from the silver salt, after treatment with ethyl iodide, yielded a white precipitate. Five grams of this salt were decomposed with boiling benzene, a slight trace of blue was observed which seemed to be obscured by the precipitate of silver halides. The benzene solution of the amorphous compound filtered

with considerable difficulty. A clear solution finally obtained on treatment with alcohol precipitated the amorphous material as a powder, some of it coming down as a gum. All of it was dissolved in chloroform and precipitated again with alcohol. A large amount of the gummy material was obtained which gradually solidified. This was used for analysis after drying. Yield of amorphous compound .8 gram.

Analysis of the Amorphous Residues

The amorphous residues prepared as described in the experimental part were analyzed for halogens by the method of Carius and electrolysis of the cyanide solution of the precipitate.

I. From the silver salt of para chlor 2,6 dibrom phenol.

Sample (a) amorphous material .1504, precipitate .2361
weight of silver .1465, Cl found 10.09 o/o, Br found 49.48 o/o,
total halogen 59.57 o/o.

Sample (b) amorphous material .1250, precipitate .1960
weight of silver .1220, Cl found 10.40 o/o, Br found 48.81 o/o,
Total halogen 59.20 o/o.

II. From the silver salt of para chlor 2,6 diiodo phenol.

Sample (a) amorphous material	.1176
weight of AgCl	.0404
weight of AgI	.1284
chlorine found	8.49 o/o
iodine found	58.98 o/o
Total	67.47 o/o

Sample (b) amorphous material	.1152
weight of AgCl	.0449
weight of AgI	.1201
chlorine found	9.63 o/o
iodine found	56.31 o/o
Total	65.94 o/o

III. From the silver salt of para brom 2,6 di-chlor phenol.

Sample (a) amorphous material	.2660
precipitate	.4608
weight of silver	.3333
chlorine found	35.82 o/o
bromine found	12.11 o/o
total	47.93 o/o

Sample (b) amorphous material	.1970
precipitate	.3415
weight of silver	.2473
chlorine found	35.99 o/o
bromine found	11.80 o/o
total	47.79 o/o

IV. From the silver salt of ortho-chlor 4,6 di-brom phenol.

Sample (a) amorphous material	.1482
precipitate	.2360
silver	.1429
chlorine found	6.90 o/o
bromine found	55.92 o/o
total halogen	62.82 o/o

Sample (b) amorphous material	.1210
precipitate	.1921
silver	.1171
chlorine found	7.78 o/o
bromine found	54.22 o/o
total halogen	62.00 o/o