

## A NEW METHOD FOR THE QUALITATIVE DETECTION OF CHLORIDES IN THE PRESENCE OF BROMIDES AND IODIDES.

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Most of the schemes for the separation of chlorides from bromides and iodides depend upon one of two general methods.

1. Most of the qualitative manuals direct the treatment of the solution of the halogens with an oxidizing agent of such a strength that iodine and bromine but not chlorine are set free. The liberated bromine and iodine may be removed from the solution by boiling, or by a current of air or by shaking out with some solvent such as carbon bisulphide. Experiments conducted by advanced students in this laboratory with this general method have been fairly successful, except that some chlorine is always set free if the reaction is carried far enough to remove all of the bromine. This method was found to be a failure in the hands of inexperienced students in qualitative analysis, perhaps on account of the necessity of exceptionally close adherence to directions.

2. The other general scheme for the separation depends upon the fact that silver chloride is soluble and silver iodide and bromide are insoluble in ammonium carbonate solution. After filtration from the undissolved silver bromide and iodide, the silver chloride is reprecipitated by neutralizing the ammonium carbonate with nitric acid. However, silver bromide, is soluble enough to produce a strong turbidity upon addition of the nitric acid. This is very confusing to the students. In addition to this trouble, the method is so very delicate that traces of chlorides which are present in most chemical reagents as impurities, will give a distinct turbidity so that the student is forced to decide from the quantity of precipitate whether chlorides have been added or not.

In the scheme described in this paper, the residue of silver chloride, bromide and iodide is treated with dilute ammonium hydroxide or carbonate, and the filtrate is treated with ammonium chloride, which will produce a turbidity or precipitate if silver chloride is present. This precipitation is caused by the action of the ion  $\text{Cl}$  from the ammonium chloride upon the common ion  $\text{Cl}$  from the silver chloride. The ammonium chloride

causes the amount of chlorine as ion in the solution to exceed the saturation concentration of the chlorine ion in equilibrium with silver, so some of the silver chloride must precipitate. Silver bromide is not affected because there is no common ion in this case.

In the following table, the ammonium hydroxide (1 : 100) solution was saturated by warming with an excess of freshly precipitated silver chloride. The ammonium chloride solution contained 25 grams per 100 cc.

Cc. of Ammonium Hydroxide-Silver Chloride Used.	Cc. of Ammonium Hydroxide (1:100) Added.	AMMONIUM CHLORIDE 25% REQUIRED TO		
		Produce a Precipitate.	Give Maximum Precipitation.	Redissolve Precipitate.
10	0	1 drop	5 drops	12 cc.
10	10	1 drop	5 drops	20 cc.
10	17	1 drop	10 drops	
10	19	5 drops		
10	20	1 cc.		

This table shows that the ammonium hydroxide silver chloride solution should be nearly saturated with the silver chloride, since large amounts of the ammonium hydroxide make precipitation impossible or very difficult.

In the following table, the ammonium hydroxide silver chloride solution was made by dissolving the silver chloride from 10 cc. of 0.8 N KCl in 100 cc. of 10 per cent. ammonium hydroxide. This solution was then diluted to 1000 with water. Each cc. of this solution contained 0.28 mg. of chloride.

Cc. of Ammonium Hydroxide Silver Chloride Used.	Cc. of Ammonium Hydroxide (1:100) Added.	AMMONIUM CHLORIDE (25%) SOLUTION REQUIRED TO	
		Produce a Precipitate	Give Maximum Precipitation
10	0	1 drop (good)	5 drops
10	10	1 drop (slight)	10 drops
10	20	2 drops (slight)	20 drops
10	30	several drops	never good
10	40	40 drops	never good

One cc. of the ammonium hydroxide silver chloride solution containing 0.28 mg. chlorine gave a good precipitate when treated with the ammonium chloride solution. Dilution of the ammonium hydroxide silver chloride solution with water did not prevent the formation of the precipitate. However, the addition of ammonium hydroxide solution made the precipitation more difficult. 0.3 mg. of chlorine as silver chloride per 10 cc. of ammonium hydroxide (1:100) does not give a precipitate when am-

monium chloride is added. This means that traces of chlorides which occur as impurities in so many reagents will not cause trouble by giving tests by this method. Smaller quantities of chlorine may be detected by using more dilute ammonium hydroxide in dissolving the silver chloride.

Corresponding solutions prepared with silver bromide in place of silver chloride gave no precipitates with ammonium chloride. In every case they produced a turbidity when acidified with nitric acid.

#### SUMMARY.

This paper describes a new method for the qualitative separation and detection of chlorides in the presence of bromides and iodides.

The mixed silver halids are digested with ammonium hydroxide (10 per cent.). The filtrate is diluted with 10 volumes of water and treated with a few drops of ammonium chloride solution. If silver chloride is present a precipitate is produced.

This method has the advantages over other methods that:

1. Bromides do not give any precipitate.
2. The concentration of the ammonium hydroxide solution is great enough that traces of chlorides occurring as impurities will not give tests. The method becomes more delicate when more dilute solutions of ammonium hydroxide are used.

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