

### 3.1: Separation of group I cations

Selective precipitation of a set of group I, i.e., lead(II) ( $\text{Pb}^{2+}$ ), mercury(I) ( $\text{Hg}_2^{2+}$ ), and silver(I) ( $\text{Ag}^+$ ) is based on soluble ions rule#3 in the solubility guidelines in section 1.1 which states "Salts of chloride ( $\text{Cl}^-$ ), bromide ( $\text{Br}^-$ ), and Iodide ( $\text{I}^-$ ) are soluble, except when the cation is Lead ( $\text{Pb}^{2+}$ ), Mercury ( $\text{Hg}_2^{2+}$ ), or Silver ( $\text{Ag}^+$ ). The best source of  $\text{Cl}^-$  for precipitating group 1 cations from a test solution is  $\text{HCl}$ , because it is a strong acid that completely dissociates in water producing  $\text{Cl}^-$  and  $\text{H}_3\text{O}^+$  ions, both do not get involved in any undesired reactions under the conditions.

The  $K_{\text{sp}}$  expression is used to calculate  $\text{Cl}^-$  that will be sufficient to precipitate group 1 cations. The molar concentration of chloride ions i.e.,  $[\text{Cl}^-]$ , in moles/liter in a saturated solution of the ionic compound can be calculated by rearranging their respective  $K_{\text{sp}}$  expression. For example, for  $\text{AgCl}$  solution,  $K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-]$  rearranges to:

$$[\text{Cl}^-] = K_{\text{sp}} / [\text{Ag}^+]$$

and for  $\text{PbCl}_2$  solution,  $K_{\text{sp}} = [\text{Pb}^{2+}][\text{Cl}^-]^2$  rearranges to:

$$[\text{Cl}^-] = \sqrt{K_{\text{sp}} / [\text{Pb}^{2+}]}$$

The concentration of ions in the unknown sample are  $\sim 0.1 \text{ M}$ . Plugging in  $0.1 \text{ M}$  value for  $\text{Pb}^{2+}$  in the above equation shows that  $[\text{Cl}^-]$  in a saturated solution having  $0.1 \text{ M } \text{Pb}^{2+}$  is  $1.3 \times 10^{-2} \text{ M}$ :

$$[\text{Cl}^-] = \sqrt{K_{\text{sp}} / [\text{Pb}^{2+}]} = \sqrt{1.6 \times 10^{-5} / 0.1} = 1.3 \times 10^{-2} \text{ M}$$

It means  $\text{Cl}^-$  concentration up to  $1.3 \times 10^{-2} \text{ M}$  will not cause precipitation from  $0.1 \text{ M } \text{Pb}^{2+}$  solution. Increasing  $\text{Cl}^-$  above  $0.013 \text{ M}$  will remove  $\text{Pb}^{2+}$  from the solution as a  $\text{PbCl}_2$  precipitate. If 99.9% removal is desired, then  $1.0 \times 10^{-4} \text{ M } \text{Pb}^{2+}$  will be left in the solution and the  $[\text{Cl}^-]$  have to be raised to  $0.40 \text{ M}$ :

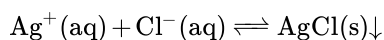
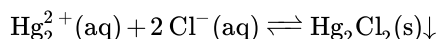
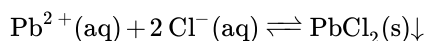
$$[\text{Cl}^-] = \sqrt{K_{\text{sp}} / [\text{Pb}^{2+}]} = \sqrt{1.6 \times 10^{-5} / 1.0 \times 10^{-4}} = 0.40 \text{ M}$$

The solubility of  $\text{Hg}_2\text{Cl}_2$  and  $\text{AgCl}$  is less than that of  $\text{PbCl}_2$ . So, a  $0.40 \text{ M } \text{Cl}^-$  will remove more than 99.9% of  $\text{Hg}_2^{2+}$  and  $\text{Ag}^+$  from the solution.

A sample of 20 drops of the aqueous solution is about  $1 \text{ mL}$ . In these experiments,  $\sim 15$  drops of the test solution are collected in a test tube and 3 to 4 drops of  $6 \text{ M } \text{HCl}$  are mixed with the solution. This results in about  $0.9 \text{ mL}$  total solution containing 1 to  $1.3 \text{ M } \text{Cl}^-$ , which is more than twice the concentration needed to precipitate out 99.9% of group 1 cations.

A concentrated reagent ( $6 \text{ M } \text{HCl}$ ) is used to minimize the dilution of the test sample because the solution is centrifuged and the supernatant that is separated by decantation is used to analyze the remaining cations. A  $12 \text{ M } \text{HCl}$  is available, but it is not used because it is a more hazardous reagent due to being more concentrated strong acid and also because if  $\text{Cl}^-$  concentration is raised to  $5 \text{ M}$  or higher in the test solution, it can re-dissolve  $\text{AgCl}$ , by forming water-soluble  $[\text{AgCl}_2]^-$  complex ion.

The addition of  $\text{HCl}$  causes precipitation of group 1 cation as milky white suspension as shown in Figure 3.1.1 and by chemical reaction equations below. The precipitates can be separated by gravity filtration, but more effective separation can be achieved by subjecting the suspension to centrifuge in a test tube. Centrifugal force forces the solid suspension to settle and pack at the bottom of the test tube from which the clear solution, called supernatant, can be poured out - a process called decantation. The precipitate is resuspended in pure water by stirring with a clean glass rod, centrifuged, and decanted again to wash out any residual impurities. The washed precipitate is used to separate and confirm the group 1 cations and the supernatant is saved for analysis of group 2, 3, 4, and 5 cations.



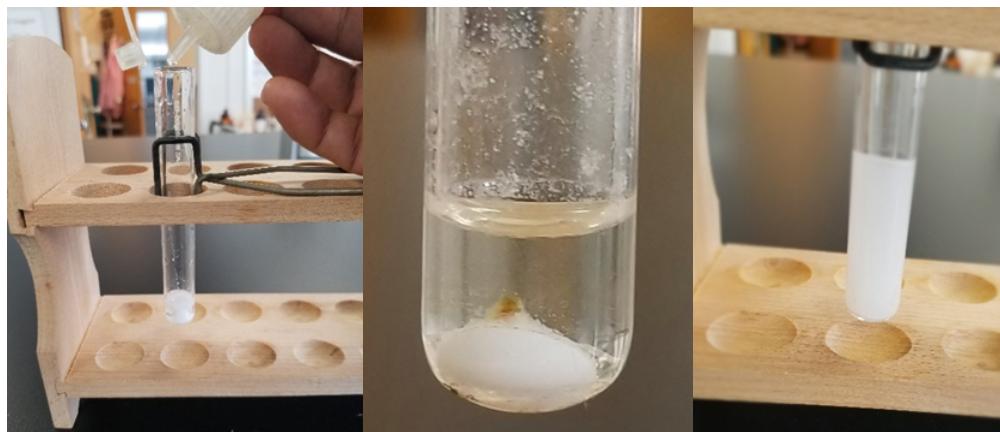


Figure 3.1.1: Precipitates of group I cations formed as a suspension upon addition of HCl drops to the test sample (left), the precipitate separated as a pellet at the bottom of the test tube by centrifugation with a clear supernatant at the top (middle), and the precipitate resuspended in washing liquid (right).

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