A MODIFIED TIN SUB-GROUP PROCEDURE

A. R. HANKE AND J. H. REEDY, *University of Illinois, Urbana, Illinois*

Introduction.—Many schemes have been proposed for the analysis of the tin sub-group but the difficulty experienced by elementary students in the analysis of this group would seem to indicate the desirability of developing a scheme of analysis which would be rugged enough to insure success even with the non-expert technique of elementary students. With this in mind, the following scheme is proposed. Table I shows the procedure in condensed form. The procedure may likewise be applied to semi-micro analysis, where the use of a centrifuge instead of filtration processes increases the speed of analysis and further simplifies the technique.

Explanatory.—It is assumed that the group II sulfides have been extracted with ammonium polysulfide, and the tin sub-group sulfides precipitated by the addition of a slight excess of HCl solution.

Separation of arsenic from tin and antimony.—The extraction of the sulfides of antimony and tin with concentrated HCl leaving arsenic sulfide in the residue (A. A. Noyes procedure) seems to be suited to the capabilities of the beginner. Usually this extraction is carried out at too high a temperature, in which case the free sulfur present will melt and form a protective layer impeding the extraction of the sulfides. A temperature of around 70° C for about 10 minutes has been found to be satisfactory.

Detection of arsenic.—In the usual scheme of analysis, the arsenic sulfide is converted into magnesium ammonium arsenate. There is no real need for this. In this scheme, the arsenic sulfide is dissolved in concentrated HNO_3, the remaining sulfur skimmed off (note 1) the solution evaporated to dryness during the dissolving process, and then treated with a few ml. of very dilute NH_4OH (note 2) plus a few drops of 3 per cent H_2O_2 (note 3). The ammonium hydroxide is neutralized with dilute acetic acid creating an ammonium acetate buffer with the solution slightly on the acid side (note 4). Silver nitrate added to this solution will then precipitate the characteristic red-brown Ag_3AsO_4 (note 5 below).

NOTES

1. The sulfur is skimmed off because it reacts with the HNO_3 forming SO_2 which in turn will reduce arsenate to arsenite.

2. If any tin is present at this point, it will be in the form of SnO_2 which has the ability to strongly absorb arsenic acid. Treating with NH_4OH brings about the desorption of the arsenic acid.

3. The H_2O_2 is added simply to insure complete oxidation of the arsenic.

4. If the solution is either ammonical or too strongly acid, the Ag_3AsO_4 will not precipitate.

5. It is best to add silver nitrate solution in excess because if any chloride or antimonate is present, its white silver salt will precipitate. This causes no harm because with excess silver nitrate, the red-brown Ag_3AsO_4 will still be detectable.

Detection of antimony and tin.—Our attention now may be turned to the antimony and tin in the concentrated HCl filtrate. It is best to boil off about one half of the HCl and then dilute back to the original volume (note 1). A good separation of antimony from tin may be affected using displacement of the antimony with sheet lead (note 2). The tin is not displaced but it is reduced to the stannous form in which condition the usual test with $HgCl_2$ may be made (note 3). The metallic antimony sloughs off the lead surface as a characteristic black curdy precipitate which is sufficient confirmation for antimony (note 4). If a double check for antimony is desired, a phosphomolydic acid test may be made on a drop of the concentrated HCl filtrate containing trivalent antimony and tetravalent tin. Phosphomolydic acid is reduced by strong reducing agents to compounds of indefinite composition but characterized by an intense blue color. The success of this test depends upon the fact that the H_2S liberated when the tin subgroup sulfides are dissolved will reduce the antimony to the trivalent state but leave the tin in the tetravalent state. This trivalent antimony is a strong enough reducing agent to give the molybdenum blue color with phosphomolydic acid. The test is best carried out as a spot test. A drop of the solution and a drop of the reagent are placed on a piece of filter paper, the filter paper being held above boiling water. For usual amounts of antimony, the boiling water technique may be left out.

Notes

1. If the HCl concentration is very high, the treatment with metallic lead will result in an unnecessarily large amount of lead in solution. The sensitivity of the $HgCl_2$ test for tin is less in concentrated HCl solution.

2. The sheet lead must be tin free. It may be cleaned by boiling with dilute HNO_3 and then washing with distilled water.

3. If a large quantity of $PbCl_2$ is formed, it will precipitate as white crystalline $PbCl_2$. This may be dissolved by warming the solution since $PbCl_2$ is quite soluble in hot water, or better yet, the solution may be cooled before the addition of $HgCl_2$ and the $PbCl_2$ filtered out.

4. If copper is present in the unknown, some of it finds its way into this HCl extract and will be deposited on the lead. It is quite different in appearance however and need not be confused with antimony. If arsenic is present in this solution, it too may be displaced. It tends to form a brown colloidal solution and hence is quite different in appearance from the black metallic antimony.

Table I—Procedure for Analysis of Tin Sub-Group

Tin Sub-Group Precipitate: As_2S_5, Sb_2S_5, SnS_2, S. Add 10 cc. of concentrated HCl. Heat to just below the boiling point for 10 minutes.

Residue: As_2S_5, S. Add 5 cc. of Conc. HNO_3 and evaporate just to dryness. During the evaporating process, the *S* may be skimmed off with a stirring rod. Add water and a few drops of NH_4OH and a few drops of H_2O_2. Boil until no odor of NH_3 is apparent. Add 2 drops of HAc and an excess of $AgNO_3$ solution. A precipitate of red-brown Ag_3AsO_4 *confirms arsenic.*	*Filtrate:* Sb^{+++}, Sn^{++++}, HCl. Boil off some of the HCl and dilute to 10 cc. Add a small piece of sheet lead and warm with periodic shaking for 10 minutes.
	Precipitate: Black curdy metallic Sb *confirms antimony.*
	Filtrate: Sn^{++} Add $HgCl_2$ solution. A satin like precipitate of Hg_2Cl_2 and Hg *indicates tin.*