

Realgar

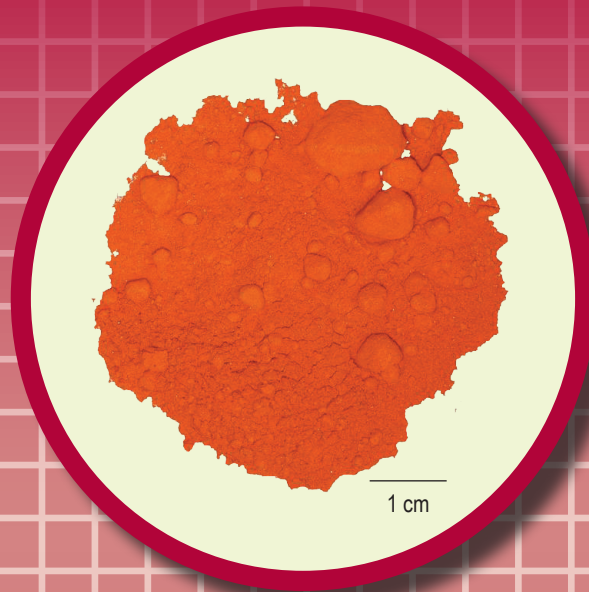


Figure 1(i) A photograph of Realgar (powders and powder aggregates)

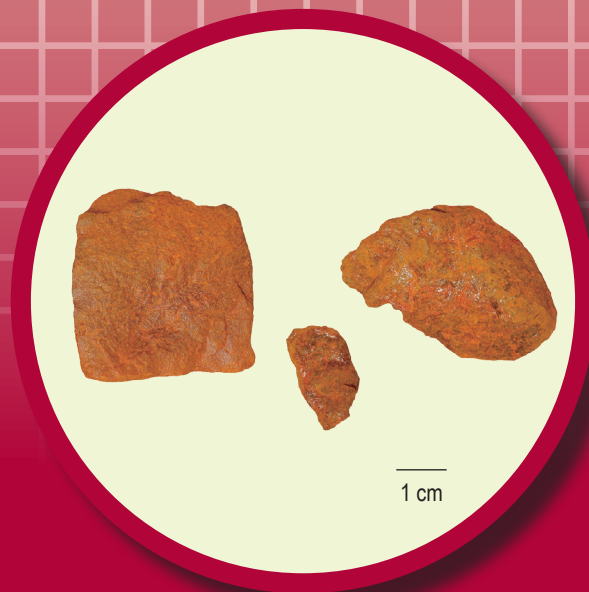


Figure 1(ii) A photograph of Realgar (lumpy)

1. NAMES

Official Name: Realgar

Chinese Name: 雄黃

Chinese Phonetic Name: Xionghuang

2. SOURCE

Realgar is a mineral of the sulphides of realgar group, containing mainly arsenic(II) sulphide (As_2S_2). The ore is collected, foreign matter removed to obtain Realgar.

3. DESCRIPTION

Aggregates of lumpy or granular masses, irregular. Orange-red to dark red, streak pale orange-red, crystal surface showing diamond-like lustre. Texture fragile, easily broken, fracture with resin-like lustre. Powder refined ore: In powders or powder aggregates, orange-yellow to orange-red. Texture lax, powdered on kneading, lustreless. Odour slightly stinking (Fig. 1).

4. IDENTIFICATION

4.1 Microscopic Identification (*Appendix III*)

Powder

Colour yellow. Irregular flakes or aggregates, golden-yellow to orange-yellow, lustrous, slightly dull in colour at the margin; minute granules dull in colour, translucent or non-transparent. Polychromatic under the polarized microscope (Fig. 2).

4.2 Physicochemical Identification

(I) Chemical test of arsenic salt

Procedure

Weigh 0.1 g of the powdered sample and place it in a 100-mL conical flask, then add 8 mL of sulphuric acid. Heat the mixture on a hot plate and boil for about 15 min. Cool down to room temperature. Transfer 1 mL of the mixture to a 250-mL conical flask. Add 20 mL of water and 2 mL of sodium hydroxide solution (40%, w/v). Add 2.0 g of sodium hydrogen carbonate and

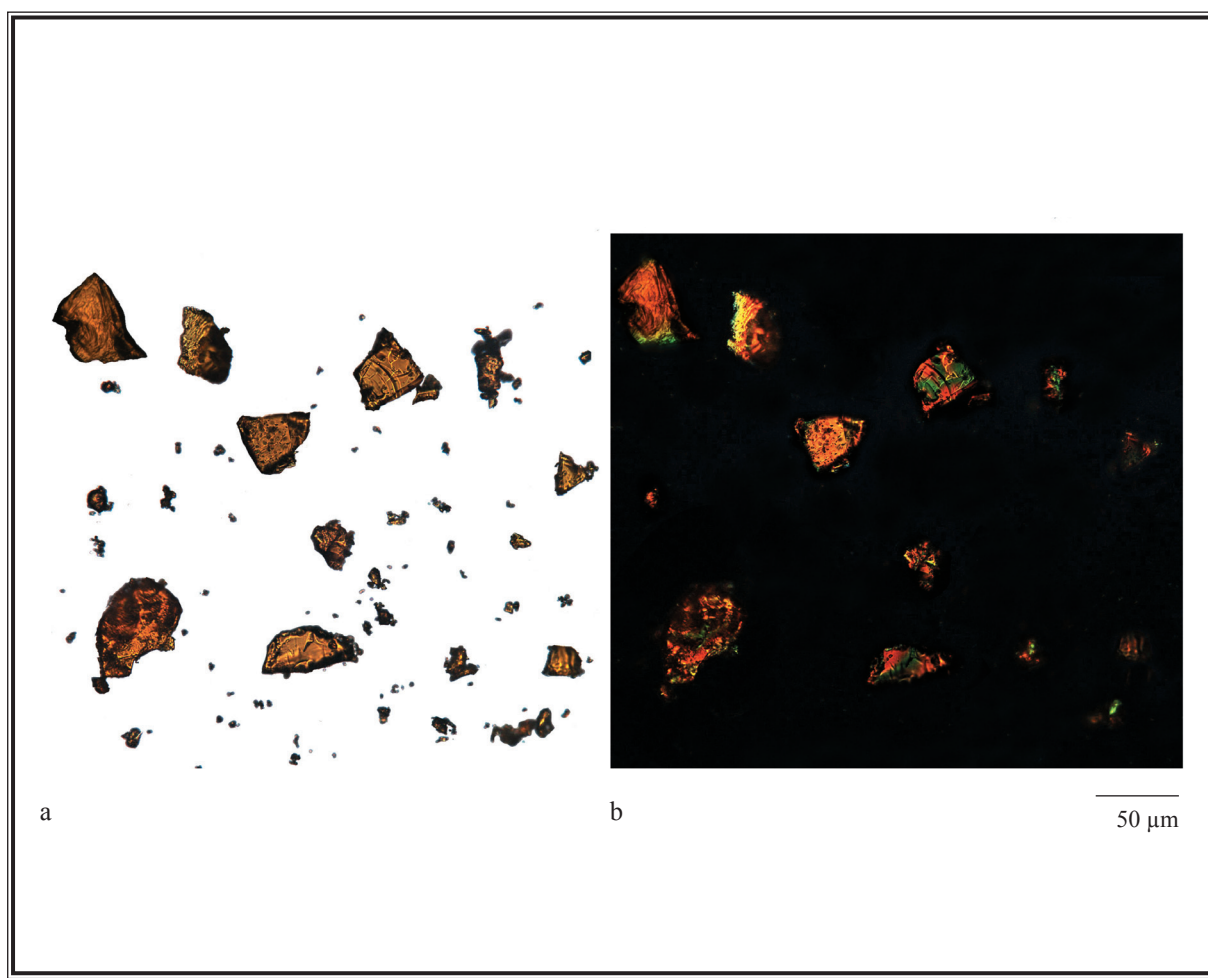


Figure 2 Microscopic features of powder of Realgar

a. Features under the light microscope b. Features under the polarized microscope

mix well. Transfer 1 mL of upper layer to a test tube. Add 1 drop of silver nitrate solution (1.7%, w/v) and mix well. Yellow precipitate can be observed.

(II) Chemical test of sulphide

Reagent

Potassium chlorate-nitric acid solution

Dissolve excess amount of potassium chlorate in nitric acid.

Procedure

Weigh 0.01 g of the powdered sample and place it in a test tube, then add 1 drop of water. Dissolve the sample in 2 mL of potassium chlorate-nitric acid solution. Add 3 drops of barium chloride solution (5%, w/v). Allow the white precipitate to settle. Discard the supernatant. Add 2 mL of water to the precipitate and mix well. White precipitate cannot be dissolved.

4.3 X-ray Powder Diffraction Pattern (*Appendix XVI*)

Carry out the method as directed in Appendix XVI.

Standard materials

Finely powdered α -Realgar (0.5 g) and β -Realgar (0.5 g).

Test sample

Weigh 0.5 g of finely powdered sample onto a glass slide or other appropriate holder. Press and smear uniformly the sample until a flat and dense solid surface is obtained.

System suitability requirements

Check the accuracy of the zero shift error (in 2θ) of the X-ray diffractometer by using certified materials (lanthanum hexaboride LaB_6 or other equivalent) at the beginning of analysis. Compare the 2θ values of characteristic diffraction peaks of such certified material with the X-ray Powder Diffraction (XRPD) pattern found in scientific standard database. The instrument is in good condition to use when each of these diffraction peaks of the certified material has a 2θ discrepancy less than $\pm 0.05^\circ$ when compared to the corresponding 2θ values of the XRPD pattern found in scientific standard database.

Procedure

Separately place the glass slide containing the finely powdered standard materials and test sample onto the diffractometer platform and record the XRPD pattern. Measure the 2θ

values of the diffraction peaks of the standard materials and test sample. Compare the 2θ values of the i) characteristic diffraction peaks of the α -Realgar standard material and test sample or ii) characteristic diffraction peaks of the β -Realgar standard material and test sample as listed in Table 1 (i) and (ii) respectively.

Table 1 (i) The 2θ values of the five characteristic diffraction peaks of α -Realgar

Peak No.	$2\theta / ^\circ$
1	14.707
2	15.451
3	16.441
4	29.297
5	30.544

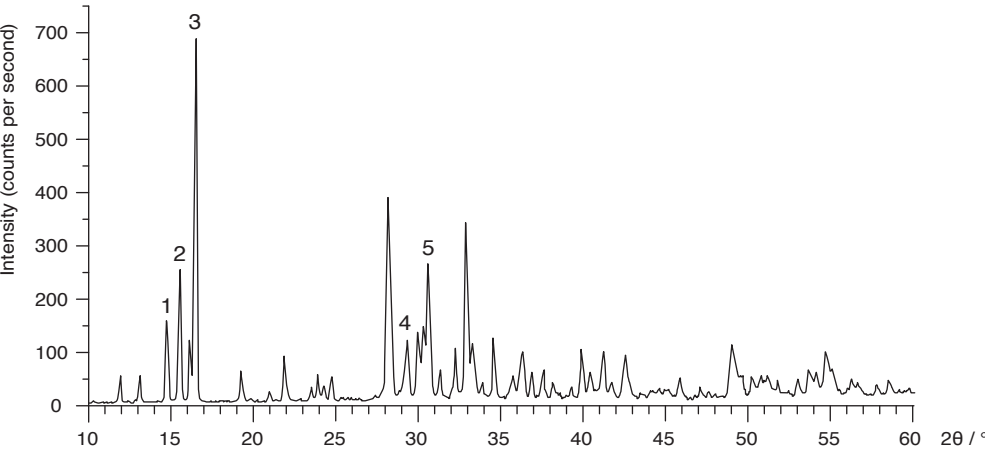


Figure 3(i) A reference XRPD pattern of α -Realgar

Table 1 (ii) The 2θ values of the five characteristic diffraction peaks of β -Realgar

Peak No.	$2\theta / ^\circ$
1	15.415
2	17.803
3	22.660
4	29.820
5	31.140

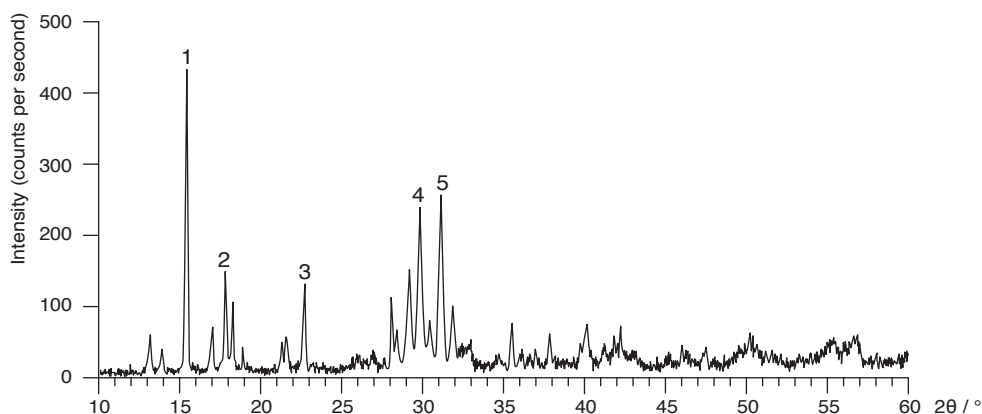


Figure 3(ii) A reference XRPD pattern of β -Realgar

For positive identification, the sample must give the above five characteristic diffraction peaks [Fig. 3(i) or (ii)] each has an angular discrepancy ($\Delta 2\theta$) less than $\pm 0.2^\circ$, compared with the values stated in Table 1 (i) or (ii).

5. TEST

Limit of arsenic (III) oxide

Reagents

Lead (II) acetate absorbent

Weigh 5.0 g of lead (II) acetate and place it in a 100-mL volumetric flask, then dissolve in water. Add acetic acid until the solution becomes clear and make up to the mark with water. Soak thoroughly 1.0 g of cotton wool in 12 mL of lead (II) acetate solution. Extrude excess solution and dry at a temperature below 100°C .

Mercuric bromide test paper

Weigh 2.5 g of mercuric bromide and dissolve in 50 mL of ethanol. Soak filter paper in mercuric bromide solution for 1 h. Dry the paper and store in the dark.

Acidic tin (II) chloride solution

Weigh 20.0 g of tin (II) chloride dihydrate and dissolve in 50 mL of hydrochloric acid.

Apparatus

A is a 100 mL conical flask with standard ground joint; B is a standard hollow ground glass stopper connected to glass conduit C (external diameter 8.0 mm, internal diameter 6.0 mm), the total length of B and C is about 180 mm, D is a plastic screw, the upper part of which has an aperture 6.0 mm in diameter and the lower part of which has an aperture 8.0 mm in diameter; E is a plastic screw cap which has an aperture 6.0 mm in diameter. A wad of lead acetate cotton wool weighing about 60 mg is packed into tube C to a depth of about 60-80 mm. A disc of mercuric bromide test paper is placed between the contacting surface of D and E.

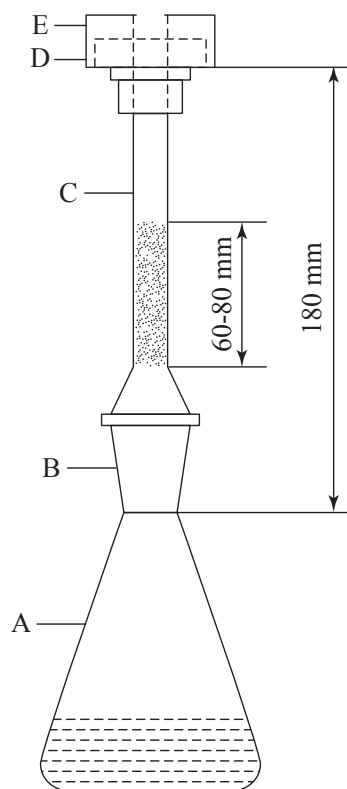


Figure 4 Apparatus for the test of arsenic (III) oxide in CMM samples

Standard solution

Arsenic (III) oxide standard stock solution, Std-Stock

Weigh 0.132 g of arsenic (III) oxide and place it in a 1000-mL volumetric flask, then add 5 mL of sodium hydroxide solution (20%, w/v). Neutralize the solution with sulphuric acid (10%, w/v) and further add 10 mL of sulphuric acid (10%, w/v). Make up to the mark with water.

Arsenic (III) oxide standard solution

Pipette 10 mL of the Std-Stock to a 1000-mL volumetric flask, then add 10 mL of sulphuric acid (10%, w/v). Make up to the mark with water. Freshly prepare the solution.

Test Solution

Weigh 1.0 g of the powdered sample and place it in a 100-mL conical flask, then add 20 mL of hydrochloric acid (28%, w/v) and stir for 30 min. Filter the mixture. Wash the residue for two times, each with 10 mL of hydrochloric acid (28%, w/v) by stirring for 10 min. Combine the extracts to a 500-mL volumetric flask and make up to the mark with water. Transfer 10 mL of solution to a 100-mL volumetric flask and make up to the mark with water.

Procedure

- (a) Transfer 2 mL of test solution to the flask (Fig. 4), add 5 mL of hydrochloric acid, 21 mL of water, 5 mL of potassium iodide solution (16.5%, w/v) and 5 drops of acidic tin (II) chloride solution.

Allow the mixture to stand for about 10 min. Add 2.0 g of zinc granule and heat the mixture on a water bath at about 40°C for 45 min. Collect and examine the mercuric bromide test paper.

- (b) Transfer 2 mL of standard solution to the flask (Fig. 4), carry out the procedure as stated in (a). Collect and examine the mercuric bromide test paper. Less intense orange spot should be observed in (a) when compared to (b).

Caution

The reaction product (arsine) is flammable, pyrophoric and poisonous.

6. ASSAY

Carry out the method as directed in Appendix XV.

Reagents

Iodine titrant

Weigh 12.69 g of iodine and 36.0 g of potassium iodide, place in a 1000-mL volumetric flask, then dissolve in water. Add 3 drops of hydrochloric acid and make up to the mark with water. Filter the solution.

Phenolphthalein indicator

Weigh 0.1g of phenolphthalein and dissolve in 10 mL of ethanol.

Starch indicator

Weigh 0.5 g of starch and dissolve in 5 mL of water. Add the mixture slowly to 100 mL of boiling water with shaking and boil for about 2 min. Cool down to room temperature. Transfer the supernatant to a 100-mL brown conical flask. Freshly prepare the indicator.

Standardization of iodine titrant

Weigh accurately 0.075 g of arsenic (III) oxide and place it in a 250-mL conical flask, then add 10 mL of sodium hydroxide solution (4%, w/v). Warm the mixture on a hot plate at about 60°C for 10 min. Add 20 mL of water and 1 drop of methyl orange indicator (1%, w/v). Neutralize the solution with sulphuric acid (5%, w/v) until the colour turns pink. Add 2.0 g of sodium hydrogen carbonate and 50 mL of water then followed by 2 mL of starch indicator. Titrate the solution with the iodine titrant until persistent purplish-blue colouration can be observed. Calculate the concentration of the iodine titrant according to the following equation:

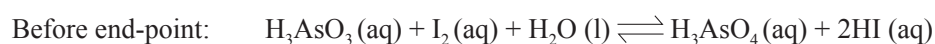
$$C_{\text{Iodine}} = \frac{W_{\text{As}_2\text{O}_3} \times P_{\text{As}_2\text{O}_3} \times 2 \times 1000}{V_{\text{Iodine}} \times \text{Mw}_{\text{As}_2\text{O}_3}}$$

- where
- C_{Iodine} = Molarity of iodine titrant (mol/L)
 - V_{Iodine} = Volume of iodine titrant used (mL)
 - $\text{Mw}_{\text{As}_2\text{O}_3}$ = Molecular weight of arsenic (III) oxide (197.84 g)
 - $W_{\text{As}_2\text{O}_3}$ = Weight of arsenic (III) oxide used (g)
 - $P_{\text{As}_2\text{O}_3}$ = Purity of arsenic (III) oxide (%)

Titration of test solution

Weigh accurately 0.1 g of the powdered sample and place it in a 250-mL conical flask, then add 1.0 g of potassium sulphate, 2.0 g of ammonium sulphate and 8 mL of sulphuric acid. Heat the mixture on a hot plate and boil for about 10 min. Cool down to room temperature. Add slowly 50 mL of water. Heat the mixture on a hot plate and boil for about 5 min. Cool down to room temperature. Add 2 drops of phenolphthalein indicator. Neutralize the solution with sodium hydroxide solution (40%, w/v) until the colour turns pink. Cool down to room temperature. Neutralize the solution with sulphuric acid (5%, w/v) until the solution turns colourless. Add 2.0 g of sodium hydrogen carbonate and 50 mL of water then followed by 2 mL of starch indicator. Titrate the solution with the iodine titrant until persistent purplish-blue colouration can be observed. Measure the volume of the iodine titrant used and calculate the percentage content of arsenic (II) sulphide in the sample by using the equation indicated in Appendix XV.

Reaction equations for Realgar:



Limits

The sample contains not less than 90.0% of arsenic (II) sulphide (As_2S_2).