CHAPTER 4

PURIFICATION OF INORGANIC AND METAL ORGANIC CHEMICALS

The commonest method of purification of inorganic species is by recrystallisation, usually from water. However, especially with salts of weak acids or of cations other than the alkaline and alkaline earth metals, care must be taken to minimise the effect of hydrolysis. This can be achieved, for example, by recrystallising acetates in the presence of dilute acetic acid. Nevertheless, there are many inorganic chemicals that are too insoluble or are hydrolysed by water so that no general purification method can be given. It is convenient that many inorganic substances have large temperature coefficients for their solubility in water, but in other cases recrystallisation is still possible by partial solvent evaporation.

Organo-metallic compounds, on the other hand, behave very much like organic compounds, e.g. they can be redistilled and may be soluble in organic solvents. A note of **caution** should be made about handling organometallic compounds, e.g. arsines, because of their **potential toxicities**, particularly when they are volatile. Generally the suppliers of such compounds provide details about their safe manipulation. These should be read carefully and adhered to closely. If in any doubt always assume that the materials are lethal and treat them with utmost care. The abbreviations are listed in Chapter 1, pp. 1 and 2. The same **safety precautions** about the handling of substances as stated in Chapter 3 should be followed here.

Acetarsol see **N-Acetyl-4-hydroxy-*m*-arsanilic acid.**

Acetonyl triphenyl phosphonium chloride and **acetylmethylene triphenyl phosphorane** see Chapter 3.

3*R*,4*R*,1'*R*-4-Acetoxy-3-[1-(*tert*-butylmethylsilyloxy)ethyl]-2-azetinone *[76855-69-1]* **M 287.4, m 107-108°, [α]$_D^{20}$+55° (c 0.5, toluene)[α]$_D^{20}$+53.7° (c 1.04, $CHCl_3$).** Purified by chromatography on silica gel (3 x 14cm) for 50g of ester using 20% EtOAc in *n*-hexane. The eluate is evaporated and the residue recrystd from hexane as white fluffy crystals. [*TET* **39** 2505 *1983*].

Acetylferrocene (ferrocenyl methylketone) *[1271-55-2]* **M 228.1, m 86°, 86-87°.** Orange-red crystals, recrystd from isooctane and sublimed at 100°/1mm. The *oxime* has **m** 167-170° (from Et_2O or aq EtOH). The *semicarbazone* has **m** 198-201° (from EtOH). [*JACS* **77** 2022 3009 *1955*; *JCS* 650 *1958*].

***N*-Acetyl-4-hydroxy-*m*-arsanilic acid** *[97-44-9]* **M 275.1.** Crystd from water.

Alizarin Red S (sodium salt, H_2O) *[130-22-3]* **M 360.3.** Commercial samples contain large amounts of sodium and potassium chlorides and sulphates. It is purified by passing through a Sephadex G-10 column, followed by elution with water, then 50% aq EtOH [King and Pruden *Analyst* **93** 601 *1968*].

Alumina (neutral) *[1344-28-1]* **M 102.0 (anhyd.).** Stirred with hot 2M HNO_3, either on a steam bath for 12h (changing the acid every hour) or three times for 30min, then washed with hot distilled water until the washings had pH 4, followed by three washings with hot MeOH. The product was dried at 270° [Angyal and Young *JACS* **81** 5251 *1959*]. For the preparation of alumina for chromatography see Chapter 1.

Aluminum acetylacetonate *[13963-57-0]* **M 324.3, m 192-194°, 195°.** Crystd several times from aqueous MeOH, λ_{max} 216 and 286mn. [*JPC* **62** 440 *1958*]. It can be purified by sublimation and has the following solubilities in g per cent: C_6H_6 35.9 (20°), 47.6 (40°), toluene 15.9 (20°), 22.0 (40°) and acetylacetone 6.6 (20°), 10.4 (40°). [*Inorg Synth* **5** 105 *1957*].

Aluminium ammonium sulphate (10H_2O) *[7784-26-1]* **M 453.3, m 93°.** Crystd from hot water by cooling in ice.

Aluminium bromide *[7727-15-3]* **M 266.7, m 97°, b 114°/10mm.** Refluxed and then distilled from pure aluminium chips in a stream of nitrogen into a flask containing more of the chips. It was then distd under vacuum into ampoules [Tipper and Walker *JCS* 1352 *1959*]. Anhydrous conditions are essential, and the white to very light brown solid distillate can be broken into lumps in a dry-box (under nitrogen). Fumes in moist air.

Aluminium caesium sulphate (12H_2O) *[14284-36-7]* **M 568.2.** Crystd from hot water (3ml/g).

Aluminium chloride (anhydrous) *[7446-70-0]* **M 133.3.** Sublimed several times in an all glass system under nitrogen at 30-50mm pressure. Has also been sublimed in a stream of dry HCl and has been subjected to a preliminary sublimation through a section of granular aluminium metal [for manipulative details see Jensen *JACS* **79** 1226 *1957*]. Fumes in moist air.

Aluminum ethoxide *[555-75-9]* **M 162.2, m 154-159°, 146-151°, b 187-190°/7mm, 210-214°/13mm.** Crystd from CS_2 [**m** 139°, complex: *ZPC* **164** 295 *1933*] and distd in a vacuum. Molecular weight corresponds to $(AlOEt_3)_4$. [*JPC* **39** 1127 *1935*; *JACS* **69** 2605 *1947*].

Aluminium fluoride (anhydrous) *[7784-18-4]* **M 84.0, m 250°.** Technical material may contain up to 15% alumina, with minor impurities such as aluminium sulphate, cryolite, silica and iron oxide. Reagent grade AlF_3 (hydrated) contains only traces of impurities but its water content is very variable (may be up to 40%). It can be dried by calcining at 600-800° in a stream of dry air (some hydrolysis occurs), followed by vacuum distn at low pressure in a graphite system, heated to approximately 925° (condenser at 900°) [Henry and Dreisbach *JACS* **81** 5274 *1959*].

Aluminium isopropoxide *[555-31-7]* **M 204.3, m 119°, b 94°/0.5mm, 135°/10mm.** Distd under vacuum. *Hygroscopic.*

Aluminium nitrate (9H_2O) *[7784-27-2]* **M 375.1.** Crystd from dilute HNO_3, and dried by passing dry nitrogen through the crystals for several hours at 40°.

Aluminium potassium sulphate (12H_2O, alum) *[7784-24-9]* **M 474.4, m 92°.** Crystd from weak aqueous H_2SO_4 (*ca* 0.5ml/g).

Aluminium rubidium sulphate (12H_2O) *[7784-29-4]* **M 496.2.** Crystd from aq H_2SO_4 (*ca* 2.5ml/g).

Aluminium sulphate *[10043-01-3]* **M 342.2, m 765°(dec).** Crystd from hot dilute H_2SO_4 (1 ml/g) by cooling in ice.

Aluminum triethyl (triethyl aluminum) *[97-93-8]* **M 114.2, b 69°/1.5mm, 76°/2.5mm, 129-131°/55mm, d$_4^{20}$ 0.695, n$_D^{20}$ 1.394.** Purified by fractionation in an inert atmosphere under vacuum in a 50cm column containing a heated nichrome spiral, taking the fraction 112-114°/27mm. It is very sensitive to H_2O and should be stored under N_2. It should not contain chloride which can be shown by hydrolysis and testing with $AgNO_3$. [*JACS* **75** 4828 5193*1953*; NMR: *JACS* **81** 3826 *1959*].

Aluminium tri-*tert*-butoxide *[556-91-2]* **M 246.3.** Crystd from benzene and sublimed at 180°.

Aluminium trimethanide (trimethyl aluminium) *[75-24-1]* **M 72.1, m 15.2°, b 111.5°/488.2mm, 124.5°/atm, d$_4^{20}$ 0.725.** Distd through a 10-20 theoretical plates column under 1 atm of N_2 (better with very slow take-off). Attacks grease (use glass joints). Also vac distd over Al in absence of grease, into small glass vials and sealed under N_2. Purity is measured by freezing point. Reacts with H_2O, is non-conducting in C_6H_6 and is **HIGHLY FLAMMABLE**. [*JCS* 468*1946*; *JACS* **68** 2204 *1946*].

4-Aminophenylmercuric acetate *[6283-24-51]* **M 371.8, m 168°, 175°(dec), 180°(dec).** Recrystd from hot dilute AcOH and dried in air. [*JICS* 32 613 *1955; A* **465** 269 *1928*].

Ammonia (gas) *[7664-41-7]* **M 17.0.** Major contaminants are water, oil and non-condensible gases. Most of these impurities are removed by passing the ammonia through a trap at -22° and condensing it at -176° under vacuum. Water is removed by distilling the ammonia into a tube containing a small lump of sodium. Also dried by passage through porous BaO, or over alumina followed by glass wool impregnated with sodium (prepared by soaking the glass wool in a solution of sodium in liquid ammonia, and evaporating off the ammonia). It can be rendered oxygen-free by passage through a soln of potassium in liquid ammonia.

Ammonia (liquid) *[7664-41-7]* **M 17.0, m -77.7°, b -33.4°, d 0.597.** Dried, and stored, with sodium in a steel cylinder, then distd and condensed by means of liquid air, the non-condensable gases being pumped off. In order to obtain liquid NH_3 from a cylinder turn the cylinder up-side-down (i.e. with the valve at the bottom, use a metal stand to secure it in this position) and lead a plastic tube from the tap to a measuring cylinder placed in an efficient fume cupboard which is kept running. Turn the tap on and allow the ammonia to be released. At first, gas and liquid will splatter out (make sure that the plastic tube is secure) but soon the liquid will drip into the measuring cylinder. The high latent heat of evaporation will cool the ammonia so that the liquid will remain cool and not boil vigorously. If the ammonia is required dry the necessary precautions should be taken, i.e. the gas is allowed to flow through tubes packed with coarse CaO pellets.

Ammonia (aqueous) *[7664-41-7]* **M 17.0 + H_2O, d 0.90 (satd, 27% w/v, 14.3 N).** Obtained metal-free by saturating distilled water, in a cooling bath, with ammonia (from tank) gas. Alternatively, can use isothermal distn by placing a dish of conc aq ammonia and a dish of pure water in an empty desiccator and leaving for several days. **AMMONIA (gas, liquid or aq soln) is very irritating and should not be inhaled as it can lead to olfactory paralysis (temporary and partially permanent).**

Ammonium acetate *[631-61-8]* **M 77.1, m 112-114°.** Crystd twice from anhydrous acetic acid, dried under vacuum for 24h at 100° [Proll and Sutcliff *TFS* **57** 1078 *1961*].

Ammonium bisulphate *[7803-63-6]* **M 115.1°.** Crystd from water at room temperature (1ml/g) by adding EtOH and cooling.

Ammonium bromide *[12124-97-9]* **M 98.0, m 450°(sublimes).** Crystd from 95% EtOH.

Ammonium chloride *[12125-02-9]* **M 53.5.** Crystd several times from conductivity water (1.5ml/g) between 90° and 0°. Sublimes.

Ammonium chromate *[7788-98-9]* **M 152.1.** Crystd from weak aqueous ammonia (*ca* 2.5ml/g) by cooling from room temperature.

Ammonium dichromate *[7788-09-5]* **M 252.1, m 170°(dec).** Crystd from weak aq HCl (*ca* 1ml/g).

Ammonium dihydrogen arsenate *[13462-93-6]* **M 159.0.** Crystd from water (1ml/g).

Ammonium dihydrogen orthophosphate *[7722-76-1]* **M 115.0, m 190°.** Crystd from water (0.7ml/g) between 100° and 0°.

Ammonium ferric oxalate ($3H_2O$) *[13268-42-3]* **M 428.1.** Crystd from hot water (0.5ml/g).

Ammonium ferric sulphate ($12H_2O$) *[7783-83-7]* **M 482.2.** Crystd from aqueous ethanol.

Ammonium ferrous sulphate ($6H_2O$) *[7783-85-9]* **M 392.1.** A soln in warm water (1.5ml/g) was cooled rapidly to 0°, and the resulting fine crystals were filtered at the pump, washed with cold distilled water and pressed between sheets of filter paper to dry.

Ammonium fluorosilicate *[16919-19-0]* **M 178.1.** Crystd from water (2ml/g).

Ammonium formate *[540-69-2]* **M 63.1, m 116°, 117.3°, d_4^{45} 1.280.** Heat solid in NH_3 vapour and dry in vacuum till NH_3 odour is faint. Recryst from abs EtOH and then keep in a desiccator over 99% H_2SO_4 *in vacuo*. It is very *hygroscopic*. Exists in two forms, stable needles and less stable plates. Also forms acid salts, i.e. $HCO_2NH_4.3HCO_2H$ and $HCO_2NH_4.HCO_2H$. [*JACS* **43** 1473 *1921*; **63** 3124 *1941*].

Ammonium hexachloroiridate (IV) *[1694-92-4]* **M 641.0.** Ppted several times from aqueous soln by saturation with ammonium chloride. This removes any palladium and rhodium. Then washed with ice-cold water and dried over conc H_2SO_4 in a vacuum desiccator. If osmium or ruthenium is present, it can be removed as the tetroxide by heating with conc HNO_3, followed by conc $HClO_4$, until most of the acid has been driven off. (This treatment is repeated). The near-dry residue is dissolved in a small amount of water and added to excess $NaHCO_3$ soln and bromine water. On boiling, iridic (but not platinic) hydroxide is ppted. It is dissolved in HCl and ppted several times, then dissolved in HBr and treated with HNO_3 and HCl to convert the bromides to chlorides. Saturation with ammonium chloride and cooling precipitates ammonium hexachloroiridate which is filtered off and purified as above [Woo and Yost *JACS* **53** 884 *1931*].

Ammonium hexacyanoferrate II hydrate *[14481-29-9]* **M 284.1.** The pale yellow trihydrate powder can be washed with 10% aq NH_3, filtd, then washed several times with EtOH and Et_2O, and dried at room temp. Decomposes in vacuum above 100° and should be stored away from light and under N_2. In light and air it decomposes by losing NH_3. [*Handbook of Preparative Inorganic Chem, (ed Brauer)* Vol II 1509 *1965*].

Ammonium hexafluorophosphate *[16741-11-0]* **M 163.0, d_4^{18} 2.181.** Crystallises from H_2O in square plates. Decomposes on heating before melting. Soluble in H_2O at 20° (74.8% w/v), also very soluble in Me_2CO, MeOH, EtOH and MeOAc and is decomposed by boiling acids. [*B* **63** 1063 *1930*].

Ammonium hypophosphite *[7803-65-8]* **M 117.1.** Crystd from hot EtOH.

Ammonium iodate *[13446-09-8]* **M 192.9.** Crystd from water (8ml/g) between 100° and 0°.

Ammonium iodide *[12027-06-4]* **M 144.9.** Crystd from EtOH by addition of ethyl iodide. Very *hygroscopic*. Stored in the dark.

Ammonium ionophore I (Nonactin) *[6833-86-7]* **M 736.9, m 147-148°,** $[\alpha]_D^{20}$ **0°** **(c 1.2, $CHCl_3$).** Crystd from MeOH in colourless needles and is dried at 20° in high vac. A selectophore with high sensitivity for NH_4^+ ions. [*HCA* **38** 1445 *1955*, **45** 129 *1962*, **55** 1371 *1972*; *Acta Cryst* **27B** 1680 *1971*].

Ammonium magnesium chloride ($6H_2O$) *[60314-43-4]* **M 256.8.** Crystd from water (6ml/g) by partial evapn in a desiccator over KOH.

Ammonium magnesium sulphate ($6H_2O$) *[20861-69-2]* **M 360.6.** Crystd from water (1ml/g) between 100° and 0°.

Ammonium manganous sulphate ($6H_2O$) *[13566-22-8]* **M 391.3.** Crystd from water (2ml/g) by partial evapn in a desiccator.

Ammonium metavanadate *[7803-55-6]* **M 117.0, m 200°(dec).** Crystd from conductivity water (20ml/g).

Ammonium molybdate *[13106-76-8]* **M 196.0.** Crystd from water (2.5ml/g) by partial evapn in a desiccator.

Ammonium nickel sulphate ($6H_2O$) *[15699-18-0]* **M 395.0.** Crystd from water (3ml/g) between 90° and 0°.

Ammonium nitrate *[6484-52-2]* **M 80.0.** Crystd twice from distilled water (1ml/g) by adding EtOH, or from warm water (0.5ml/g) by cooling in an ice-salt bath. Dried in air, then under vacuum.

Ammonium oxalate (H_2O) *[6009-70-7]* **M 142.1.** Crystd from water (10ml/g) between 50° and 0°.

Ammonium perchlorate *[7790-98-9]* **M 117.5.** Crystd twice from distilled water (2.5ml/g) between 80° and 0°, and dried in a vacuum desiccator over P_2O_5. Drying at 110° might lead to slow decomposition to chloride. **POTENTIALLY EXPLOSIVE.**

Ammonium reineckate *[13573-16-5]* **M 345.5, m 270-273°(dec).** Crystd from water, between 30° and 0°, working by artificial light. Solns of reineckate decompose slowly at room temperature in the dark and more rapidly at higher temperatures or in diffuse sunlight.

Ammonium selenate *[7783-21-3]* **M 179.0.** Crystd from water at room temperature by adding EtOH and cooling.

Ammonium sulphamate *[7773-06-0]* **M 114.1, m 132-135°.** Crystd from water at room temperature (1ml/g) by adding EtOH and cooling.

Ammonium sulphate *[7783-20-2]* **M 132.1, m 230°(dec).** Crystd twice from hot water containing 0.2% EDTA to remove metal ions, then finally from distilled water. Dried in a desiccator for two weeks over $Mg(ClO_4)_2$.

Ammonium tetrafluoroborate *[13826-53-0]* **M 104.8.** Crystd from conductivity water (1ml/g) between 100° and 0°.

Ammonium tetraphenylborate *[14637-34-4]* **M 337.3, m *ca* 220°(dec).** Dissolve in aqueous Me_2CO and allow crystn to proceed slowly otherwise very small crystals are formed. No trace of Me_2CO was left after drying at 120° [*TFS* **53** 19 *1957*]. The salt was ppted from dilute AcOH soln of sodium tetraphenylborane in the presence of NH_4^+ ions. After standing for 5min, the ppte was filtered off onto a sintered porcelain crucible, washed with very dilute AcOH and dried at room temp for at least 24h [*AC* **28** 1001 *1956*]. Alternatively a soln of sodium tetraphenylborane (5% excess) in H_2O is added to NH_4Cl soln. After 5min the ppte is collected, washed several times with H_2O and recryst from aqueous Me_2CO. [*ACA* **19** 342 *1958*].

Ammonium thiocyanate *[1762-95-4]* **M 76.1, m 138°(dec).** Crystd three times from dilute $HClO_4$, to give material optically transparent at wavelengths longer than 270nm. Has also been crystd from absolute MeOH and from acetonitrile.

Ammonium tungstate *[11120-25-5]* **M 283.9.** Crystd from warm water by adding EtOH and cooling.

Ammonium (meta) vanadate *[7803-55-6]* **M 117.0, d_{10}^{20} 2.326.** Wash with H_2O until free from Cl^- and dry in air. It is soluble in H_2O (5.18g/100 at 15°, 10.4g/100 at 32°) but is more soluble in dilute NH_3. When heated at relatively low temperatures it loses H_2O and NH_3 to give vanadium oxide (V_2O_5) and at 210° it forms lower oxides. [*Inorg Synth* **3** 117 *1950*].

***n*-Amylmercuric chloride** *[544-15-0]* **M 307.2, m 110°.** Crystd from EtOH.

9,10-Anthraquinone-2,6-disulphonic acid (disodium salt) *[84-50-4]* **M 412.3, m >325°.** Crystd three times from water, in the dark [Moore et al. *JCSFT1* **82** 745 *1986*].

9,10-Anthraquinone-2-sulphonic acid (sodium salt, H_2O) *[131-08-8]* **M 328.3.** Crystd from water using active charcoal.

Antimony (V) pentafluoride *[7783-70-2]* **M 216.7, m 7.0°, 8.3°, b 141°, 150°, 148-150°, d 2.99.** Purified by vacuum distillation preferably in a quartz apparatus, and stored in quartz or aluminum bottles. It is a *hygroscopic* viscous liquid which reacts *violently* with H_2O and is hydrolysed by alkalis. *It is* **POISONOUS** *and attacks the skin.* [*JCS* 2200 *1950*; *Handbook of Preparative Inorganic Chemistry (ed Brauer)* Vol I 200 *1965*].

Antimony trichloride *[10025-91-9]* **M 228.1, m 73°, b 283°.** Dried over P_2O_5 or by mixing with toluene or xylene and distilling (water is carried off with the organic solvent), then distd twice under dry nitrogen at 50mm, degassed and sublimed twice in a vacuum into ampoules. Can be crystd from CS_2. Deliquescent. Fumes in moist air.

Antimony trifluoride *[7783-56-4]* **M 178.8, m 292°.** Crystd from MeOH to remove oxide and oxyfluoride, then sublimed under vacuum in an aluminium cup on to a water-cooled copper condenser [Woolf *JCS* 279 *1955*].

Antimony triiodide *[7790-44-5]* **M 502.5, m 167°.** Sublimed under vacuum.

Antimony trioxide *[1309-64-4]* **M 291.5, m 656°.** Dissolved in minimum volume of dilute HCl, filtered, and six volumes of water were added to ppte a basic antimonous chloride (free from Fe and Sb_2O_5). The ppte was redissolved in dilute HCl, and added slowly, with stirring, to a boiling soln (containing a slight excess) of Na_2CO_3. The oxide was filtered off, washed with hot water, then boiled and filtered, the process being repeated until the filtrate gave no test for chloride ions. The product was dried in a vacuum desiccator [Schuhmann *JACS* **46** 52 *1924*].

Argon *[7440-37-1]* **M 39.95, b -185.6°.** Rendered oxygen-free by passage over reduced copper at 450°, or by bubbling through alkaline pyrogallol and H_2SO_4, then dried with $CaSO_4$, $Mg(ClO_4)_2$, or Linde 5A molecular sieves. Other purification steps include passage through Ascarite (asbestos impregnated with sodium hydroxide), through finely divided uranium at about 800° and through a -78° cold trap.
Alternatively the gas is passed over CuO pellets at 300° to remove hydrogen and hydrocarbons, over Ca chips at 600° to remove oxygen and, finally, over titanium chips at 700° to remove nitrogen. Also purified by freeze-pump-thaw cycles and by passage over sputtered sodium [Arnold and Smith *JCSFT 2* **77** 861 *1981*].

o-**Arsanilic acid** *[2045-00-3]* **M 216.1, m 153°,**
p-**Arsanilic acid** *[98-50-0]* **M 216.1, m 232°.** Crystd from water or ethanol/ether.

Arsenazo I *[520-10-5]* **M 614.3, ε 2.6 x 10^4 at 500nm, pH 8.0.** A saturated aqueous soln of the free acid was slowly added to an equal volume of conc HCl. The orange ppte was filtered, washed with acetonitrile and dried for 1-2h at 110° [Fritz and Bradford *AC* **30** 1021 *1958*].

Arsenazo III *[1667-00-4]* **M 776.4.** Contaminants include monoazo derivatives, starting materials for synthesis and by-products. Partially purified by pptn of the dye from aqueous alkali by addition of HCl. More thorough purification by taking a 2g sample in 15-25ml of 5% aq NH_3 and filter. Add 10ml HCl (1:1) to the filtrate to ppte the dye. Repeat procedure and dissolve solid dye (0.5g) in 7ml of a 1:1:1 mixture of *n*-propanol:conc NH_3:water at 50°. After cooling, filter soln and treat the filtrate on a cellulose column using 3:1:1 mixture of *n*-propanol:conc NH_3:water as eluent. Collect the blue band and evaporate to 10-15ml below 80°, then add 10ml conc HCl to ppte pure Arsenazo III. Wash with EtOH and air-dry [Borak et al. *Talanta* **17** 215 *1970*]. The purity of the dye can be checked by paper chromatography using M HCl as eluent.

Arsenic *[7440-38-2]* **M 74.9, m 816°.** Heated under vacuum at 350° to sublime oxides, then sealed in a Pyrex tube under vacuum and sublimed at 600°, the arsenic condensing in the cooler parts of the tube. Stored under vacuum [Shih and Peretti *JACS* **75** 608 *1953*].

Arsenic tribromide *[82868-10-8]* **M 394.6, m 89°/11mm, 221°/760mm.** Distd under vacuum.

Arsenic trichloride *[60646-36-8]* **M 181.3, b 130.0°.** Refluxed with arsenic for 4h, then fractionally distd. The middle fraction was stored with sodium wire for two days, then again distd [Lewis and Sowerby *JCS* 336 *1957*].

Next Page