

Practical Lesson No 2
ANALYSIS OF AMALGAM AND CEMENT
DEMONSTRATION OF FLUORIDE IN TOOTHPASTE

1 ANALYSIS OF AMALGAM

1.1 Theory

Mercury, Hg, is a metallic element with a remarkable property of being liquid at ambient temperature (melting point $-39\text{ }^{\circ}\text{C}$, boiling point $357\text{ }^{\circ}\text{C}$). Metallic mercury is a poison; even exposition to mercury vapours at room temperature can lead to chronic intoxication. Inorganic compounds of mercury contain either mercury(II), Hg^{2+} , or mercury(I), Hg_2^{2+} . Example of the former class is mercury(II) chloride, HgCl_2 (sublimite), soluble in water and highly poisonous; while the latter group is represented by mercury(I) chloride, Hg_2Cl_2 (calomel), which is insoluble in water and hence non-toxic. At favourable conditions mercury(I) salts disproportionate to mercury(II) salt and a metallic mercury.

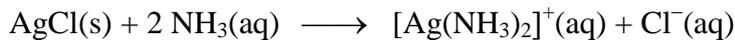
Liquid metallic mercury is able to dissolve other metals; the resulting alloy is called an amalgam. This phenomenon has been known from ancient time; it was once used to extract gold or silver from their ores, or to gild metallic objects in fire. Not all metals, however, are soluble in mercury. Amalgamation is easily achieved with sodium, potassium, zinc, cadmium, gold or tin, while higher temperature is necessary to dissolve copper or silver, and iron, cobalt and nickel can only be amalgamated by electrolysis.

The dental-filling amalgam is prepared by making a suitable metal alloy first; its fine filings are then dissolved in mercury. Nowadays, the major component of dental amalgam is silver, Ag (the alloy is at its hardest and most firm when contains 70 % of Ag) and tin, Sn. In order to decrease the volume changes of amalgam filling during its hardening, copper, Cu, is added into the alloy (4.5 % on average) and also zinc, Zn, (1 % on average). The plasticity of amalgam during its preparation is affected by the amount of mercury used; while time required for amalgamation and hardening depends on the alloy composition, and also on the fineness of the filings.

1.2 Procedure:

- a. Measure 1-2 portions of powdered dental-filling amalgam (containing, as described above, Ag, Sn, Hg, Zn, and possibly Cu) into a test tube and add about 5 ml of diluted HNO_3 . Heat it in a water bath up to boiling. Grey amalgam gradually dissolves as all the metals form their respective nitrates. Simultaneously a grey-white precipitate appears – it is stannic acid H_2SnO_3 (or, more correctly, hydrated polymeric $\text{Sn}(\text{IV})$ oxide, $\text{SnO}_2 \cdot n\text{H}_2\text{O}$), product of oxidation of Sn^{4+} .
- b. Prepare three other test tubes for filtrations. Let the heated tube cool down, and filter into test tube No 1. The grey-white precipitate of stannic acid on the filter is evidence of tin.

- c. Into the filtrate (i.e. the solution that passed the filter) in tube No 1 add several drops of diluted hydrochloric acid, HCl. White precipitate appears – now it is mixture of silver(I) chloride, AgCl, and mercury(I) chloride, Hg₂Cl₂ (calomel). Filter off this precipitate into test tube No 2, and keep both the filter and the filtrate for further steps.
- d. Dissolve some solid potassium ferricyanide, K₃[Fe(CN)₆] in distilled water. Add this solution into the filtrate in test tube No 2; the resulting ochre colour is zinc ferricyanide, i.e., it is evidence of Zn²⁺ ions.
- e. Pour about 2 ml of aqueous ammonia, NH₄OH, onto the filter with precipitated chlorides, and collect the filtrate again (test tube No 3). Silver and mercury chlorides can now be differentiated: while silver ions are solubilised by ammonia and pass the filter:

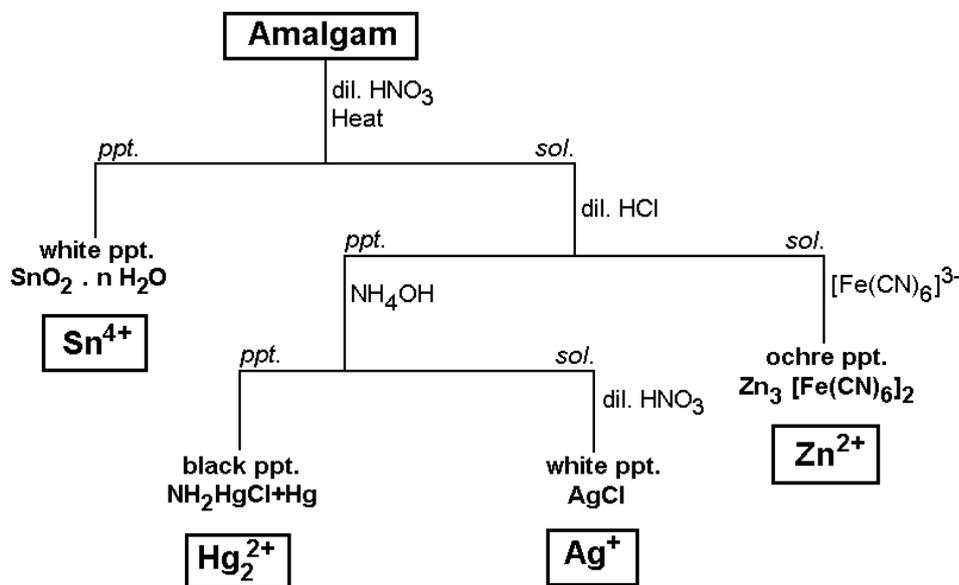


mercury(I) chloride disproportionates:



The mixture of mercury(II) amido chloride and metallic mercury forms the black or grey precipitate on the filter – evidence of Hg₂²⁺. If the amalgam contains a higher amount of copper, the filter will now also be blue due to formation of a complex compound of copper with ammonia.

- f. Add diluted HNO₃ to the last filtrate containing ammonia complex of silver chloride. Acidification results in precipitation of silver chloride again – evidence of Ag⁺:



2 ANALYSIS OF DENTAL CEMENT

2.1 Theory

Dental cements:

Powder:	Liquidum:			
	Phosphoric acid	Polyalkenoic acids	Eugenol (ethoxybenzoic acid)	Ester of salicylic acid
ZnO (MgO) (+ Ag, Cu)	Zinc oxide-phosphate cements	Carboxylic cements	Zinc oxide-eugenol cements (ZOE)	-
Silicate Glass	Silico-phosphate cements (SPC)			
	Silicate cements (SC)	Glass-ionomer cements (GIC)	-	-
Ca(OH) ₂	-	-	-	Calcium salicylate cements

Silicate Cement:

	Powder:				Liquidum:		
	Type I		Type II			typical contents	range
	typical contents	range	typical contents	range			
SiO ₂	45 %	30-47 %	38 %	32-42 %	H ₃ PO ₄	42 %	38-48 %
Al ₂ O ₃	33 %	21-33 %	30 %	21-36 %	AlPO ₄	10 %	0-10 %
CaO	12 %	0-14 %	-	-	Zn ₃ (PO ₄) ₂	8 %	15-20 %
Na ₃ PO ₄ , Ca ₃ (PO ₄) ₂	8.7 %	6-10 %	8 %	6-16 %	H ₂ O	40 %	28-44 %
Na ₂ CO ₃	2 %	2-7 %	-	-			
CaF ₂ , NaF	-	-	24 %	13-35 %			

The classical silicate dental cement is prepared by mixing together powdered silicate glass (calcium silicate containing also alumina and fluoride ions) and the liquidum, containing phosphoric acid. The mixture hardens in several minutes due to an acid-base reaction between phosphoric acid and the glass particles yielding matrix of insoluble calcium and alumina phosphates (recall that tooth mineral, actually, is calcium phosphate/hydroxide).

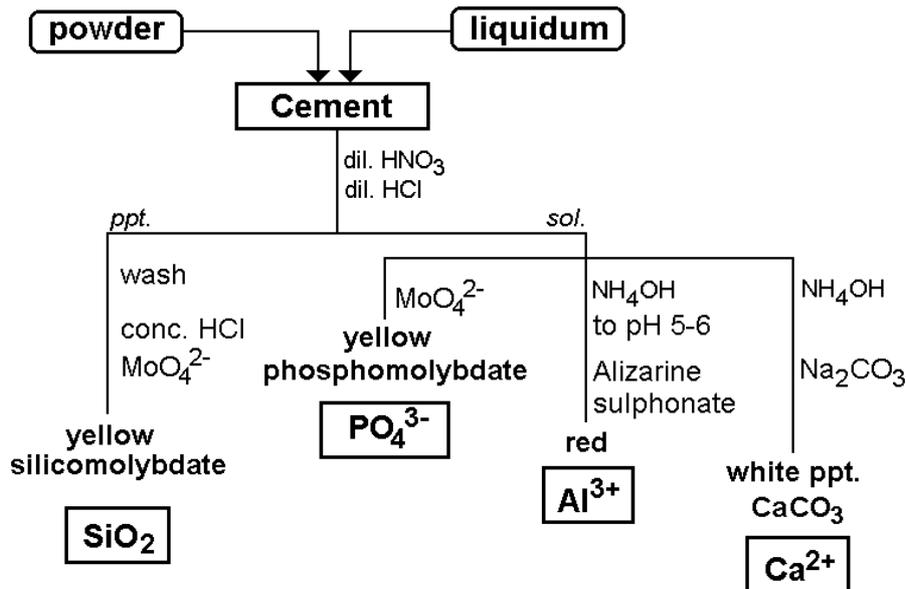
Nowadays, usage of the old silicate cement has been largely replaced by a new class of materials – glass-ionomer cements. They consist of particles of silicate glass just as in silicate cement, but the liquid phase is a polyalkenoic (e.g., polyacrylic) acid rather than phosphoric acid. Hardening is a complex process of ion exchange between solid and liquid phase, first an early matrix is made of calcium-polyalkenate bonds, and later much stronger and more stable bonds between alumina ions and polyalkenate prevail. An essential new quality of a glass-ionomer cement is that polyalkenate also replaces phosphate from dentin; the released phosphate is in turn absorbed by the glass particles. In other words, a chemical bond occurs between the cement and the dental tissue, and this interaction typically is stronger than bonds occurring in the cement itself. The glass-ionomers display an excellent biocompatibility. In addition, the ion exchange during cement hardening also causes release of fluoride ions from glass particles; they can diffuse out to the surrounding dental tissues and so promote remineralization (see below) and also inhibit bacterial growth, hence, provide a permanent local protection from tooth decay.

On the other hand, the glass-ionomers have some weak points, limiting their usage: the process of hardening is prone to volume changes due to water exclusion/absorption, maturation of cement lasts relatively long time, poor aesthetic qualities, and mechanical resistance relatively low compared to composite materials (organic polymers). In an effort to develop material devoid of these pitfalls while preserving the good points of glass-ionomers, resin-modified glass-ionomers have appeared. Resin monomers, whose polymerization is often started by illumination (“light-curing”), are added to the formula. The light-induced resin polymerization starts the overall process of material hardening and protects the slower acid-base cement hardening reaction from changes in water content; hardening also is faster, making work with material more convenient.

An extremely wide array of these materials appears recently as their development continues; detailed discussion of their properties and usage in dentistry is by far beyond the scope of this lesson. In this practical, you will prepare a glass-ionomer cement and perform a qualitative demonstration of its major inorganic components.

2.2 Procedure:

- a. Preparation of cement: Measure 3 portions of the powder onto a glass plate, and add 3 drops of the *liquidum*. Combine and rub together using a clean and dry stainless-steel spatula. At ambient temperature the cement hardening lasts about 3-5 minutes.
- b. Peel off the clod of hard cement into a beaker. Add 8 ml of diluted HNO₃ and 2 ml of diluted HCl. Allow to dissolve; the remaining precipitate is a mixture of silicic acids of various hydration state. Filter off this precipitate. Both the filtrate and the filter will be used for further analysis.
- c. Wash the precipitate on the filter twice with distilled water (discard this filtrate). Take the filter out from the funnel, fold out, place between two other sheets of filter paper, and press gently. Put the filter onto a watch glass and drop with concentrated HCl and solution of ammonium molybdate. A yellow colour of silicomolybdate acid results – evidence of silica.
- d. The solution (filtrate) from the first filtration is to be divided into three parts.
- e. Into the first part add some ammonium molybdate solution. The bright yellow colour/precipitate is phosphomolybdate – evidence of phosphate.
- f. Neutralize the second part of the filtrate to pH 5-6 (by dropwise addition of ammonium hydroxide and checking the pH with a pH paper) and combine with solution of sodium alizarine sulphonate. The filtrate solution containing colloid alumina hydroxide turns red – evidence of Al³⁺.
- g. Alkalize the rest of the filtrate with ammonium hydroxide and then add sodium carbonate solution. The white precipitate of CaCO₃ is evidence of Ca²⁺.



3 FLUORIDE IN TOOTHPASTE

3.1 Theory

The tooth enamel is composed of a hydroxyapatite (calcium phosphate/hydroxide) of formula $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{Ca}(\text{OH})_2$ or $\text{Ca}_5(\text{PO}_4)_3\text{OH}$. In the pathogenesis of tooth decay, bacteria living on the tooth surface metabolise sugar to organic acids. The resulting acidic medium gradually dissolves the tooth mineral as H^+ combines with OH^- from the hydroxyapatite, producing a cavity in the tooth.

If, however, fluoride anion, F^- , is allowed to replace the OH^- in the tooth mineral, the resulting fluoroapatite, $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$ or $\text{Ca}_5(\text{PO}_4)_3\text{F}$ is much more resistant to acidic pH than hydroxyapatite. That's why the impregnation of teeth with fluoride provides protection from tooth decay. Oral administration of fluoride pills may however be harmful since analogous reaction of fluoride with hydroxyapatite in bones is not beneficial; rather, a local application is preferred. Most brands of toothpaste sold nowadays contain fluoride either as simple sodium fluoride, NaF , sodium monofluorophosphate, or even more complex aminofluorides (see figure). The fluoride in complex compounds should display better bioavailability compared to sodium fluoride.

