

Dental Amalgam and Other Restorative Materials

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Amalgam Capsules

- Contain (in separate compartments):
 - powdered amalgam alloy
 - liquid mercury
- Some are manually activated, others self-activated
- Pestle usually included



Amalgamator (Triturator)

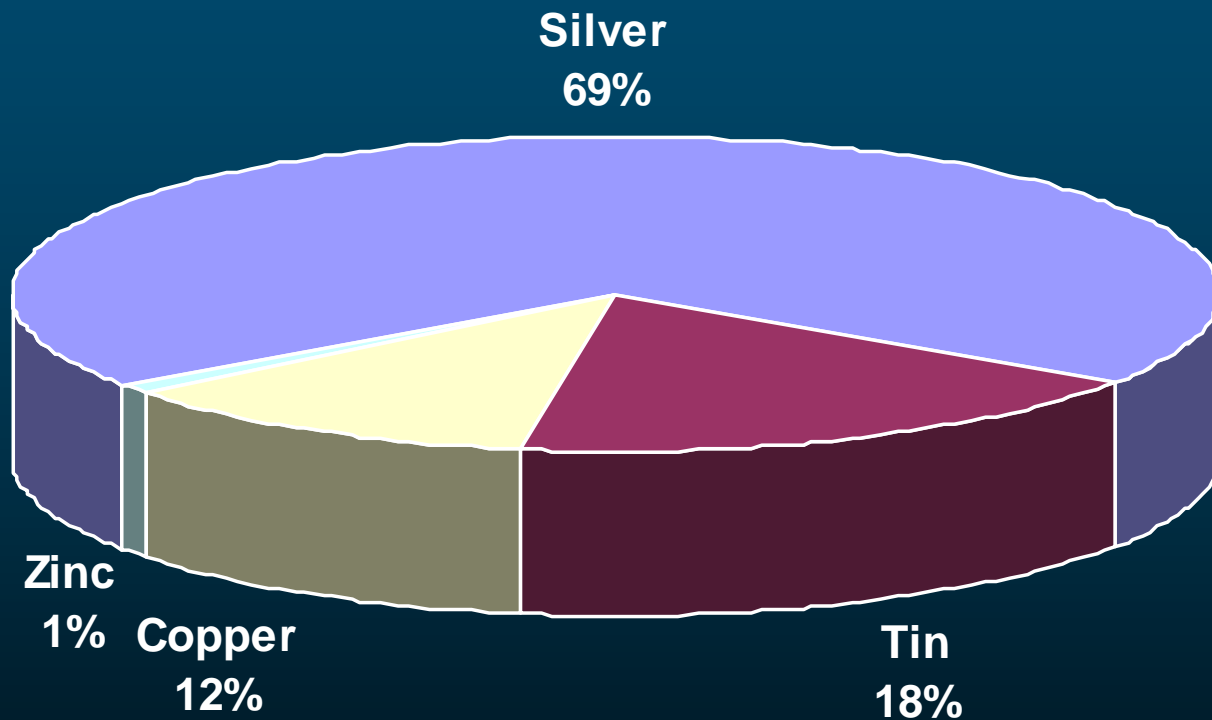
- Speeds vary upward from 3000 rpm
- Times vary from 5–20 seconds
- Mix powder and liquid components to achieve a pliable mass
- Reaction begins after components are mixed



Types of Dental Amalgam

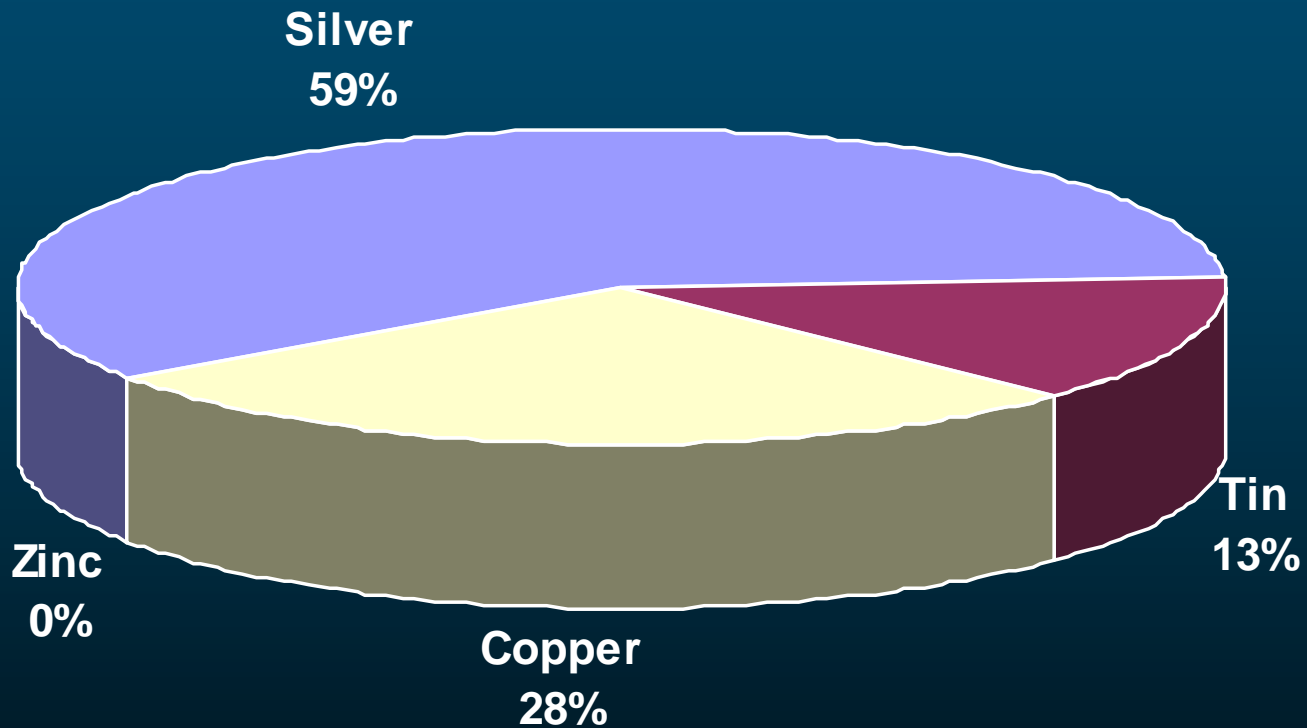
- Copper amalgam (no longer used)
- Conventional (low-copper) amalgam: formulation standardized in 1890's
- High copper amalgam: first developed in the 1960's

Alloy Powder: Dispersalloy[®]



Mixing proportions: 50% alloy, 50% mercury

Alloy Powder: Tytin[®]



Mixing proportions: 57.5% alloy, 42.5% mercury

What is Amalgam?

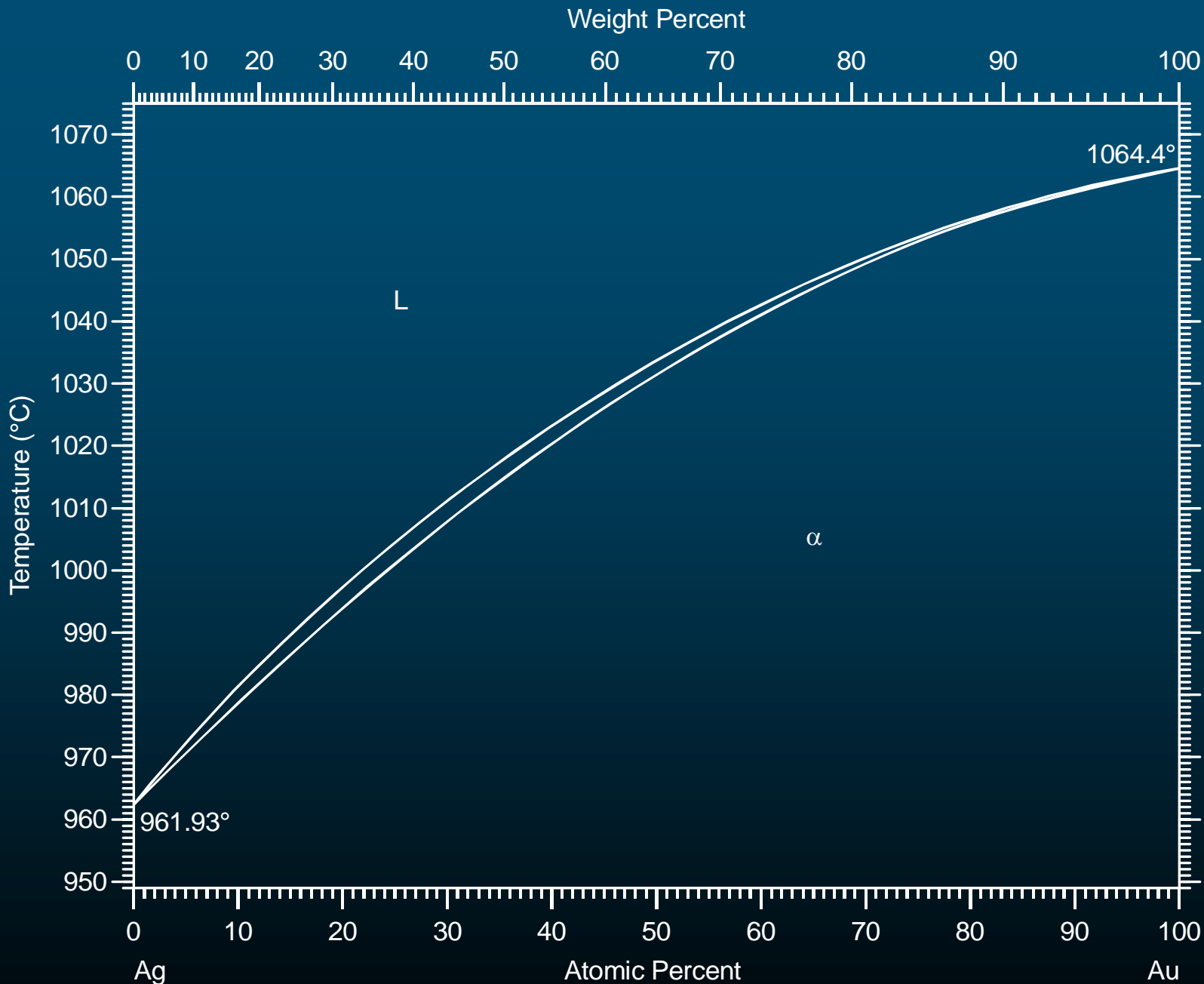
“any alloy of mercury with another metal or other metals [*silver amalgam* is used as a dental filling]”*

**Webster’s New World Dictionary of the American Language*, Guralnik DB, Ed., New York: World Publishing Co., 1972

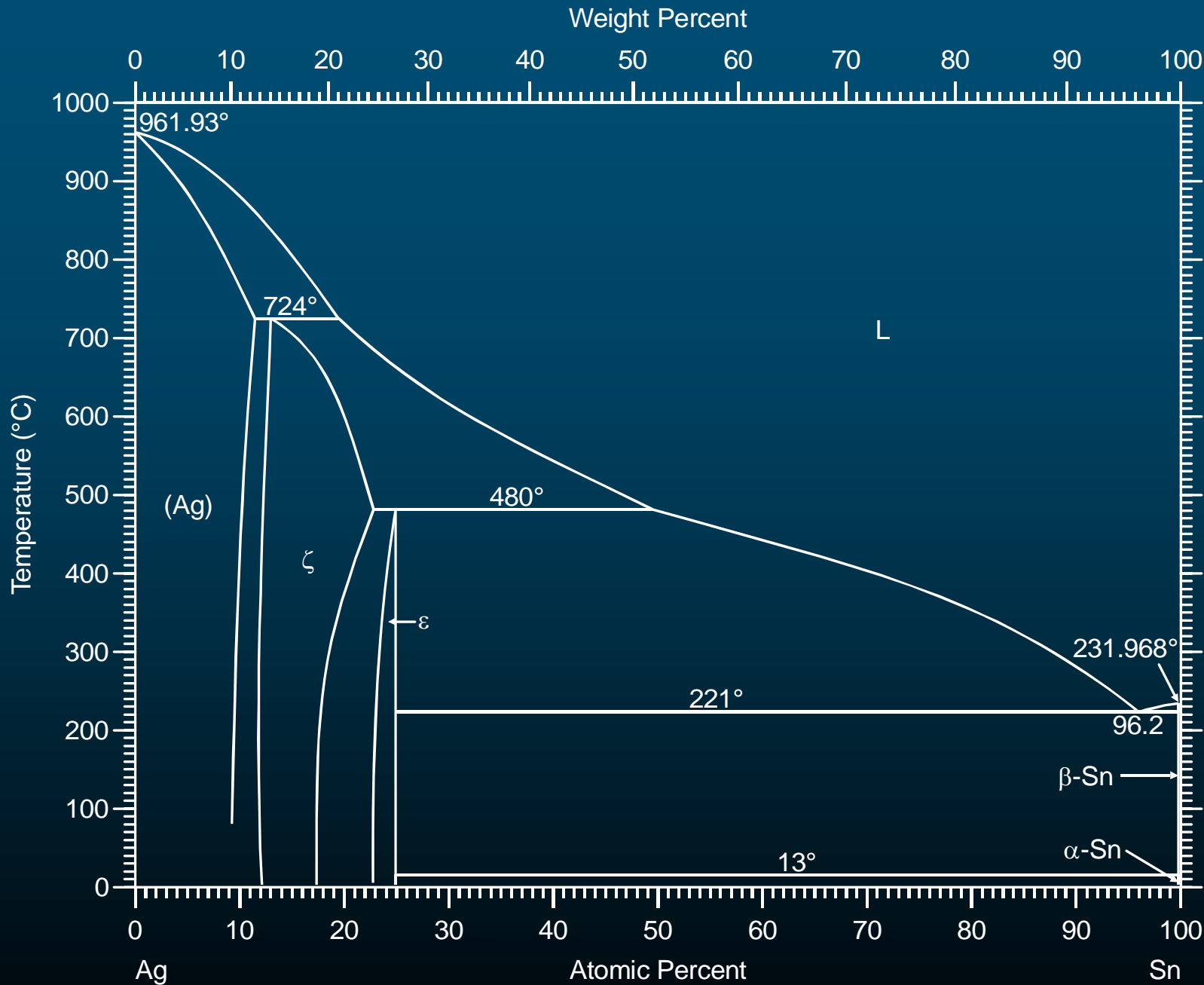
“an alloy of mercury”†

†*McGraw-Hill Dictionary of Scientific and Technical Terms*. New York: McGraw-Hill Book Company, 1974

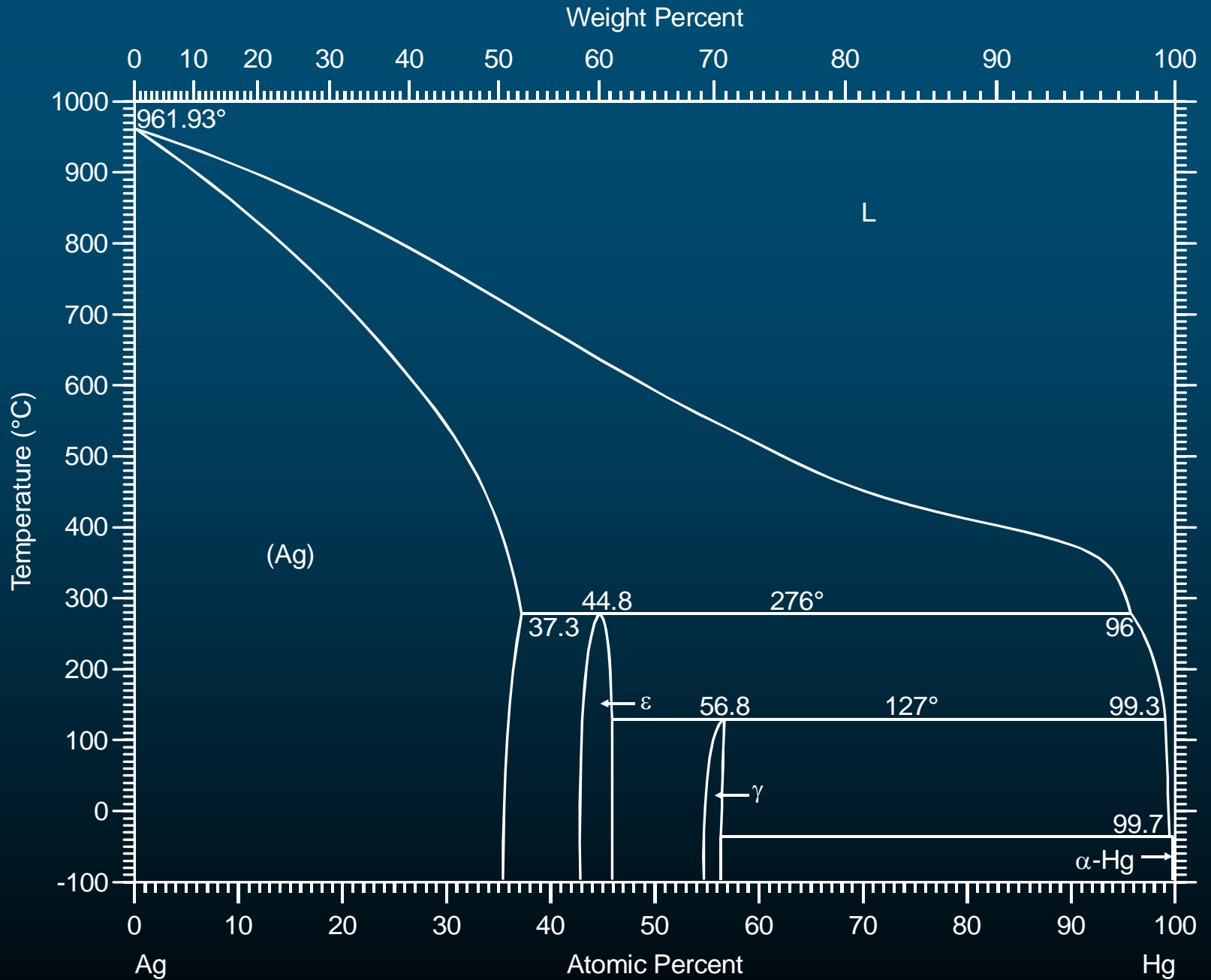
Silver-Gold Phase Diagram



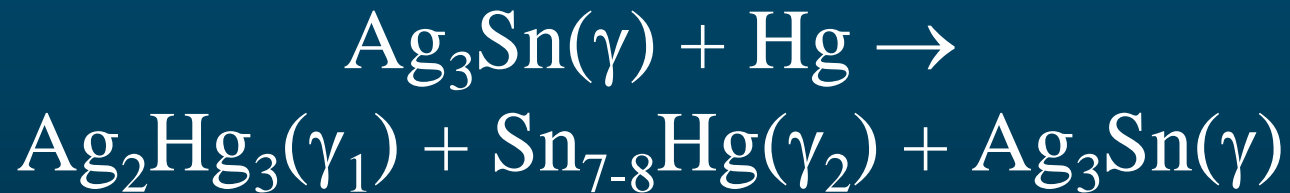
Silver-Tin Phase Diagram



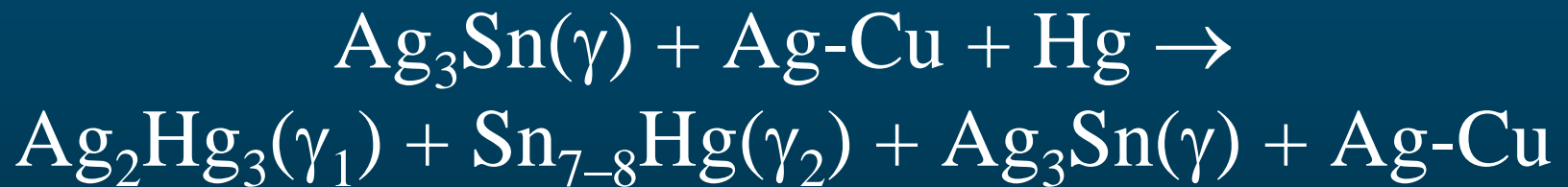
Silver-Mercury Phase Diagram



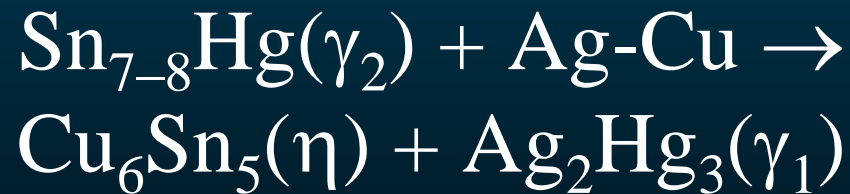
Reaction: Low-Copper Alloys



Reaction: High-Copper Alloys



and



Dental Amalgam Summary

- Powder is silver-tin-copper (Ag-Sn-Cu) alloy, with small amounts of other elements, depending on brand
- Liquid is elemental mercury (Hg)
- Mercury dissolves and reacts with Ag-Sn-Cu alloy to form intermetallic compounds, including “gamma-1” phase (Ag_2Hg_3)
- There is no free Hg in set amalgam

Composition of Set Amalgam

- Matrix of γ_1 (Ag_2Hg_3) and η (Cu_6Sn_5) phases, with embedded particles of unreacted γ (Ag_3Sn) and Ag-Cu phases
- Not a “solid emulsion” or “mixture”

Misunderstanding → Controversy

- Belief that amalgam is a kind of mixture—a “solid emulsion”—has led to much of the current controversy
- “...it is not correct to refer to an aggregate of intermetallic compounds, all of which are solid at room temperature, as a solid emulsion.” —Laurier Schramm, author of *Dictionary of Colloid and Interface Science*.

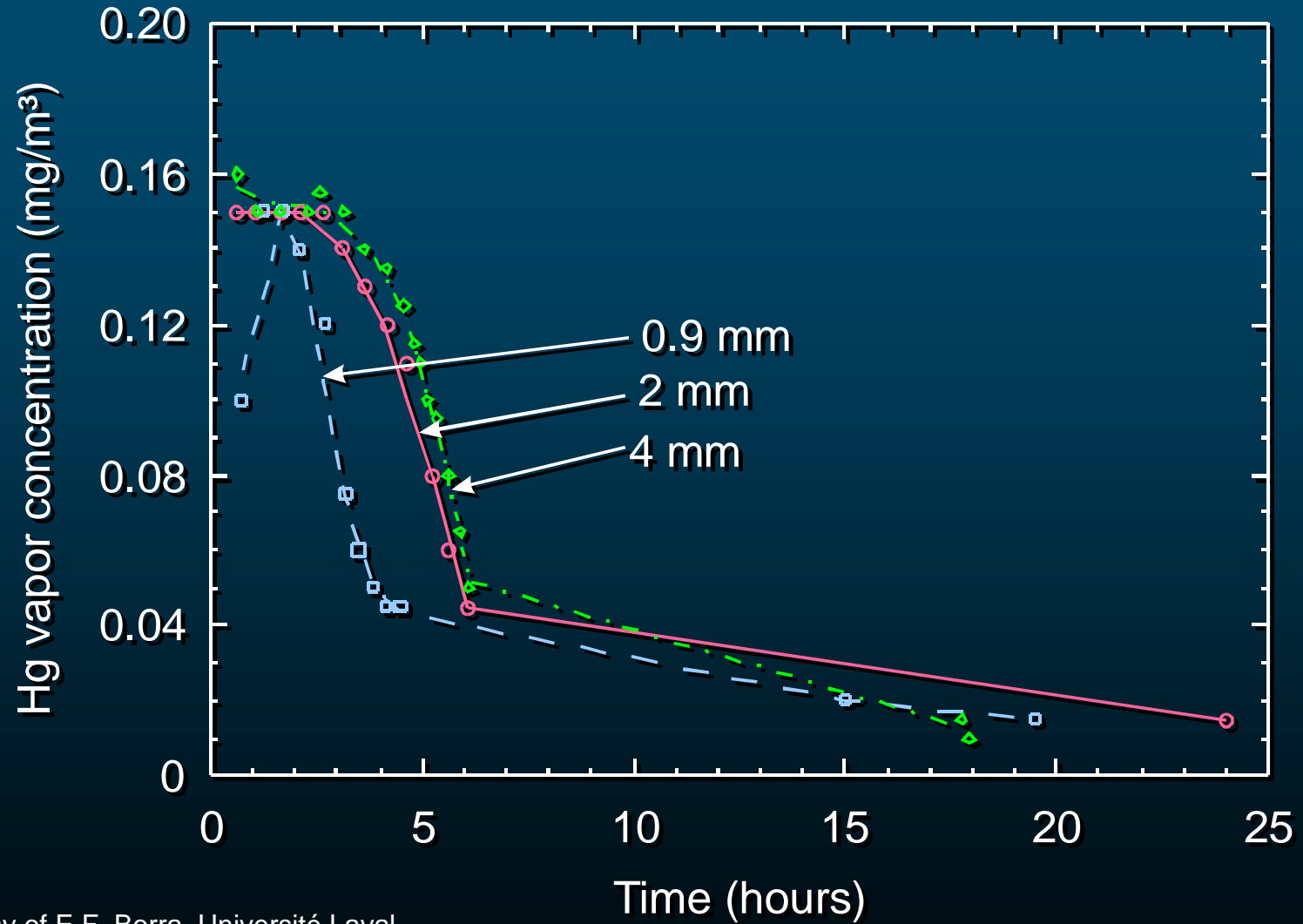
Properties of Mercury

- Only liquid metal at room temperature
- Evaporation rate (Langmuir's equation)
 - At 20°C, theoretical maximum is
 $58 \mu\text{g}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$
 - At 37°C, theoretical maximum is
 $229 \mu\text{g}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$
 - Oxidation of Hg lowers rate by factor of 1000

Université Laval 3.7-m LMT



Mercury vapor concentration as function of time



If Amalgam Were a Mixture...

- Vapor pressure above mixtures is given by Raoult's law (mixture components contribute according to their mole fractions)
- If it were a mixture, amalgam would have a Hg vapor pressure of 0.0016 torr at 37°C (about one-third that of liquid mercury)
- At this vapor pressure, amalgam would emit Hg at $76 \mu\text{g}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ (Langmuir's equation)

Hg Evaporation from Amalgam

- Baseline Hg vaporization rate (unstimulated) from amalgam in humans is $0.027 \text{ ng}\cdot\text{cm}^2\cdot\text{s}^{-1}$
- Average vaporization rate (over 24-h period) in humans is $0.048 \text{ ng}\cdot\text{cm}^2\cdot\text{s}^{-1}$
- The evaporation rate of Hg from amalgam is over *4 million* times lower than from unoxidized, liquid mercury

Hg Evaporation from Amalgam

- The evaporation rate predicted assuming amalgam is a mixture is $76 \mu\text{g}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$
- The measured evaporation rate of Hg from amalgam is $0.048 \text{ ng}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$
- The measured evaporation rate of Hg from amalgam is *1.6 million* times lower than that predicted assuming amalgam is merely a mixture

Amalgam and Mercury

1950's – 1970's

- Frykholm Study, 1957 (no detectable mercury in organs of animals after 9 weeks)
- Svare, Frank, and Chan Study, 1972 (vapor undetectable over amalgam after 400 minutes)
- McNerny, Buseck, and Hanson, 1972 (gold-film mercury vapor detector developed)
- Gay, Cox, and Reinhardt, 1979 (first demonstration of mercury release from set amalgam)

Mercury Detection by Means of Thin Gold Films

Abstract. *The adsorption of elemental mercury vapor on a thin (several hundred angstroms) gold film produces resistance changes in the film. An instrument for the detection of mercury based on this phenomenon is simple and rapid and requires no chemical separations other than passage of the vapor sample through a few standard dry filters. The instrument is portable, and the technique is directly applicable to environmental problems and geochemical prospecting. The limit of detection of the prototype instrument is 0.05 nanogram of mercury.*

In recent years much attention has been devoted to the development of methods for the detection of low concentrations of Hg, both for environmental studies and for geochemical prospecting. A portable instrument capable of rapid, inexpensive analysis is desirable for these purposes. Most semi-portable devices for the detection of low concentrations of Hg have relied on the atomic absorption technique. A variety of modifications have been described, all based on the fact that Hg absorbs at 2537 Å (1, 2). A serious limitation, however, is the presence of interfering substances such as H₂O, O₃, SO₂, and a variety of organic compounds and fine particulates (2). These absorb or scatter electromagnetic energy in the spectral region of interest. As a result of the efforts made to overcome these interferences, the resulting instruments have lost either their portability or their sensitivity, or both.

We have developed an extremely

sensitive and portable Hg detector (3) based on the phenomenon that a thin Au film undergoes a significant increase in resistance upon the adsorption of Hg vapor. This resistance change is linear in nanogram concentrations.

Gold films are prepared by vacuum evaporation on ceramic or glass substrates in a conventional high-vacuum system (10⁻⁶ torr) with the use of a Cr underlayer and no substrate heating. After preparation, the films are an-

into the flow path of the instrument. If the sample is already a vapor, it is injected with a syringe through a rubber septum (B in Fig. 1). This method of introduction can be modified to permit continuous sampling, thereby bypassing the hypodermic introduction.

Before the carrier gas enters the film chamber, the gas is scrubbed of H₂O vapor and acid vapors such as H₂S in a filter train containing MgClO₄ and Ascarite. The airstream is then divided into two fractions. One fraction is scrubbed of Hg by passage over PdCl₂ (5) before it enters the reference chamber. The other fraction is passed over the sensing film. Changes in the resistance of the sensing film are due to Hg adsorption, and variations in the film resistance due to thermal fluctuations or other adsorbing gases are neutralized.

Two factors which affect the sensitivity of the instrument are film thick-

Table 1. Precision data for the Au-film Hg detector; S.D., standard deviation.

Hg vapor standard	Amount of Hg		S.D. (ng)	S.D. (%)	99% tolerance interval (ng)	Determinations (No.)
	Mean (ng)	Range (ng)				
1	0.5	0.47- 0.53	0.03	6	0.09	17
2	1.1	1.05- 1.17	.04	4	.12	16
3	2.2	2.1 - 2.3	.07	3	.21	16
4	3	2.8 - 3.2	.13	4	.39	16
5	11	10.2 -12.0	.62	6	1.9	15
6	25	21.1 -29.2	2.6	10	8.0	15

Jerome Mercury Vapor Analyzer



- Designed to measure mercury vapor where room volume \gg sample volume
- Differences in sampling volumes and flow rates must be taken into account, or gross errors will result

Room Air: Jerome Instrument

250 mL



0 $\mu\text{g}/\text{m}^3$

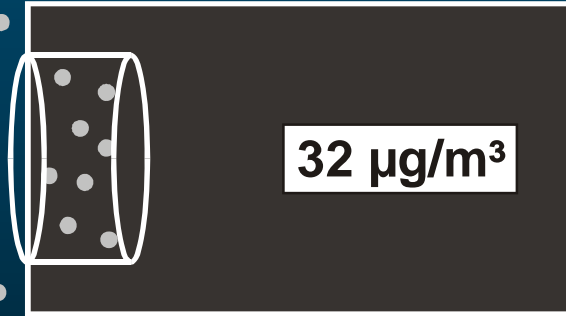
32 $\mu\text{g}/\text{m}^3$

0 sec



Room Air: Jerome Instrument

250 mL



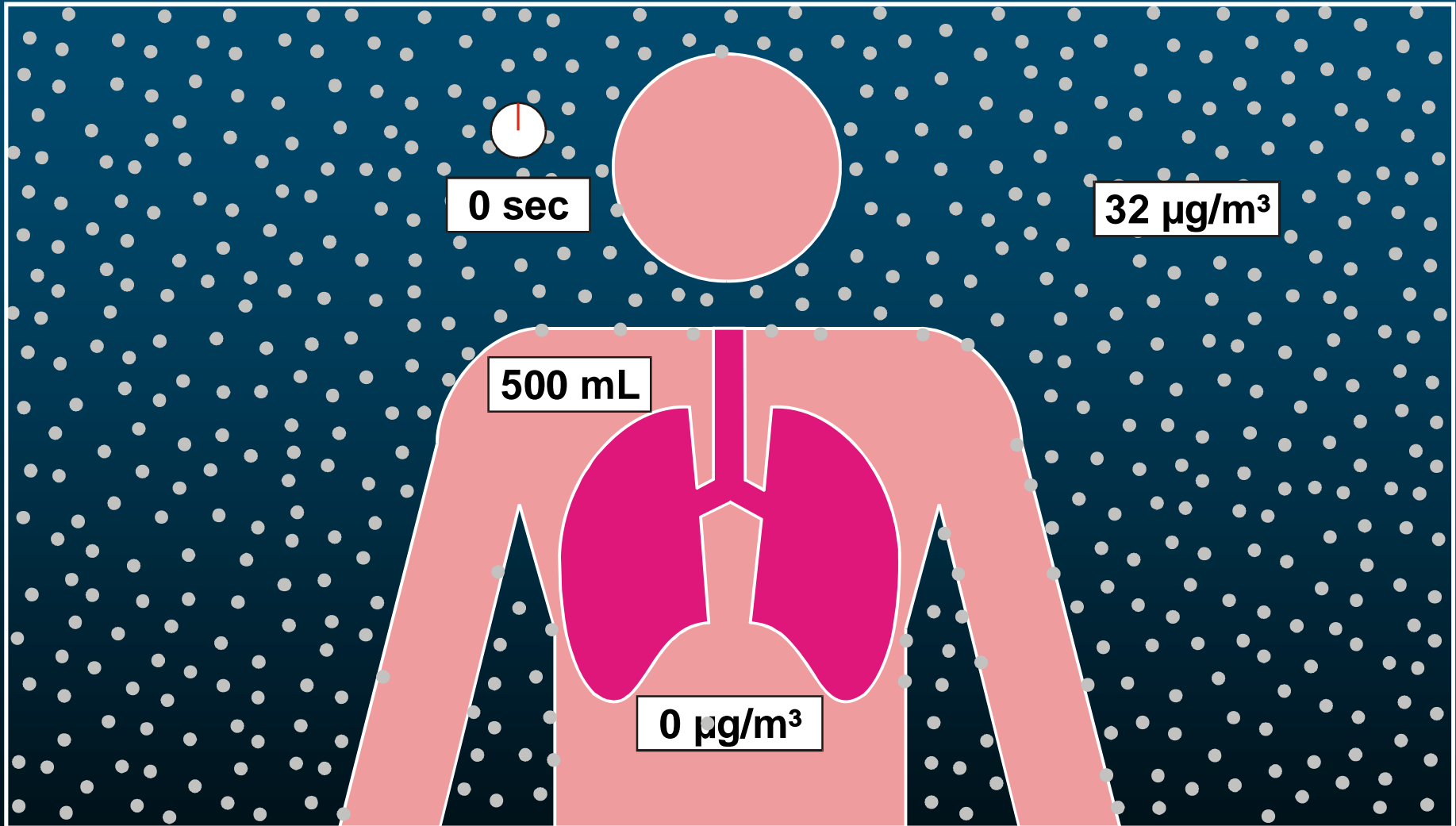
32 µg/m³

32 µg/m³

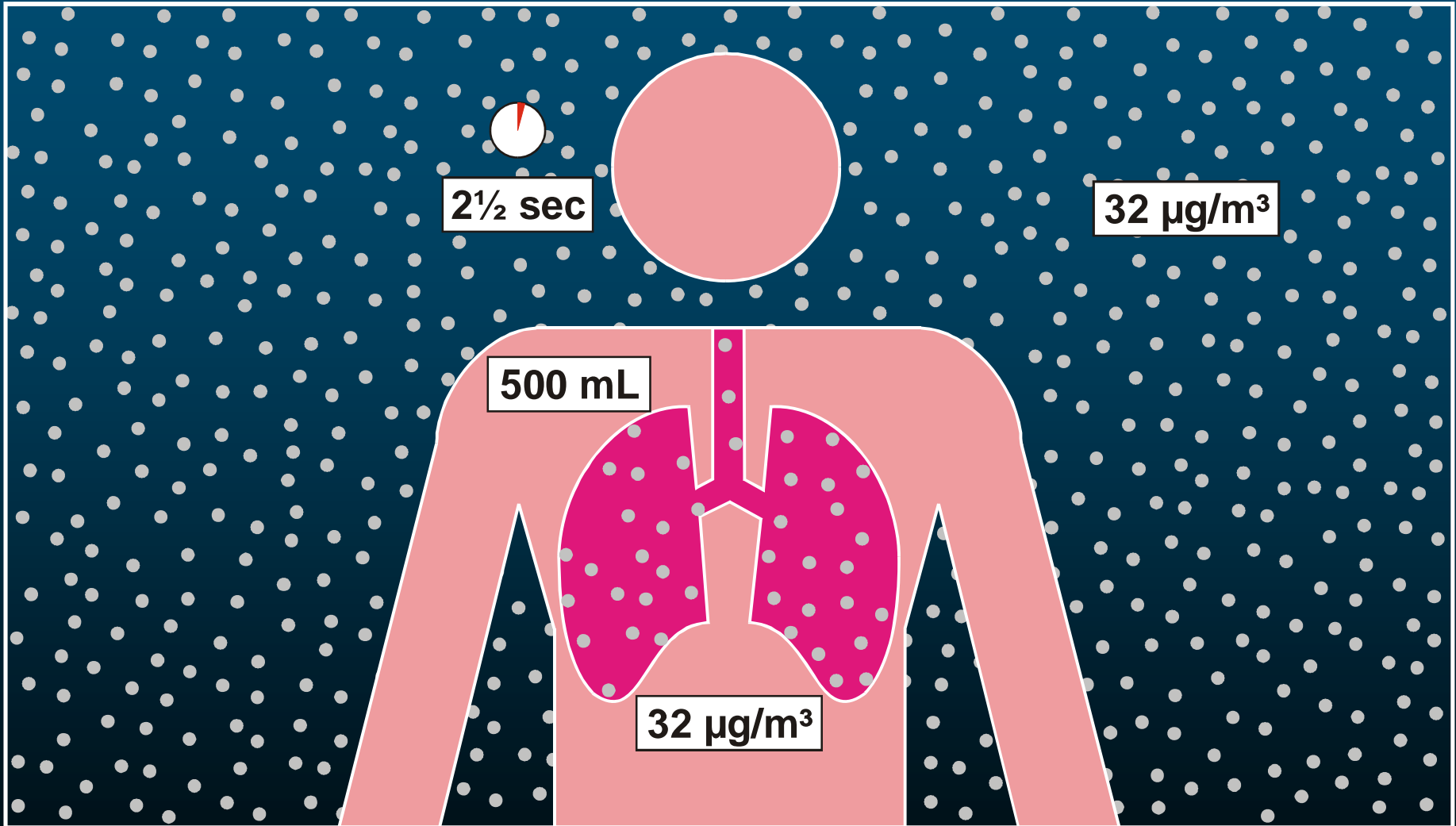


20 sec

Room Air: Human Respiration



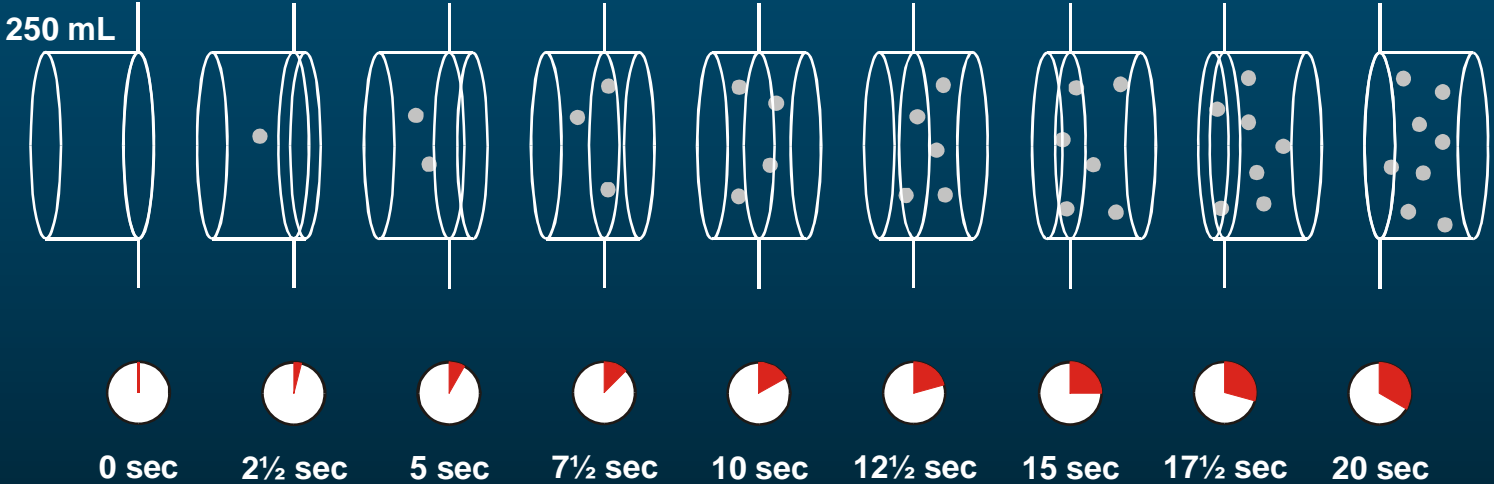
Room Air: Human Respiration



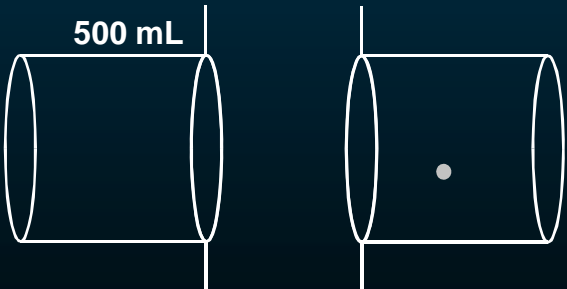
Intra-Oral Air

Jerome Instrument vs. Human Respiration

**Jerome Instrument
(20 sec)**



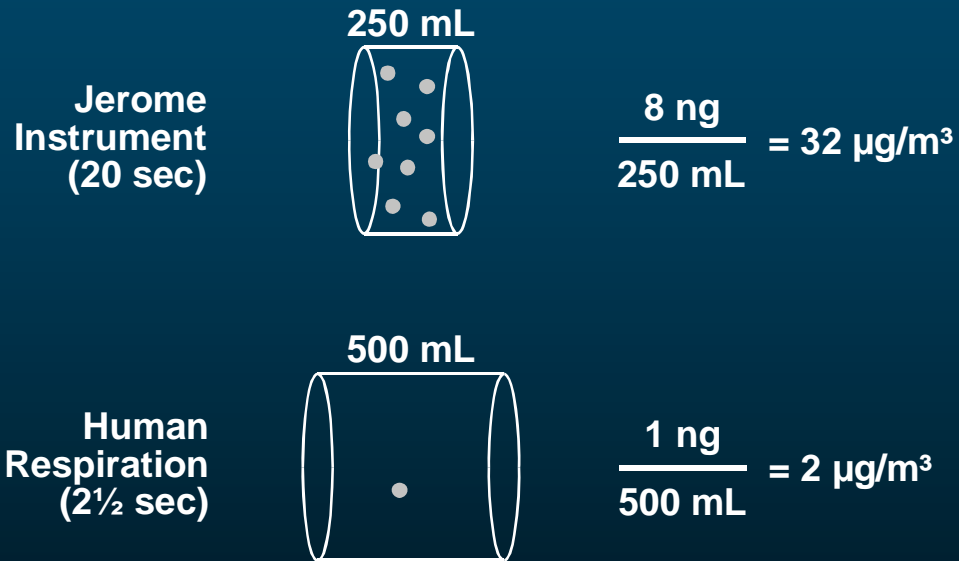
**Human Respiration
(2½ sec)**



• 1 ng Hg

Intra-Oral Air

Jerome Instrument vs. Human Respiration



- 1 ng Hg

Intra-Oral Mercury Vapor Measurements—Summary

- The instrument is designed to measure mercury vapor in a room, where the volume of air is large compared to the sample volume
- Volume and flow rate issues cause the Jerome instrument to over-estimate the mercury concentration by *at least* a factor of 16 if these are not taken into account

Other Factors

- Mercury accumulation in the oral cavity:
Each second of delay will cause the meter reading to be an additional 5% too high
(Mackert, 1987)
- Interferences can be detected as mercury:
garlic, *etc.* (Newman, 1987)

Alternatives to Amalgam

Restoration Longevity

- Difficult to measure because of selection bias
- A retrospective study of restoration longevity almost always suffers from the effects of selection
- Another problem with retrospective studies is that often only failed restorations are analyzed and not restorations *in situ*

Amalgam and Composite: Retrospective Studies

- 2001 study: median age of over 1800 failed amalgam restorations was nearly 12 years but slightly less than 5 years for over 1500 failed resin composite restorations
- 2000 study of 6761 replaced restorations: median age of replaced amalgam was 10 years, but that of composite was only 8 years

Amalgam and Composite: Retrospective Studies

- 1999 study of over 9000 restorations: showed that amalgam outlasted resin composite for class 1, 2, and 5 restorations
- 1998 study: showed the median age of a replaced amalgam restoration was 15 years versus only 8 years for a replaced resin composite

Amalgam and Composite: Retrospective Studies

- 2002 study of insurance claims database: 207,000 replaced amalgam, 93,000 replaced composite restorations; found that resin composites were significantly more likely to fail than amalgams

Amalgam and Composite: Prospective Studies

- No prospective clinical studies comparing amalgam and composite restoration longevity, *per se*, have been performed
- The Casa Pia study (DeRouen *et al.*, 2006) showed that after 5 years, “the need for additional restorative treatment was approximately 50% higher in the composite group.”

Composites: Clinical Issues

- “Packable” composites have not been shown to yield better proximal contacts than conventional composites (Peumans *et al.*, 2001)
- Even with the newest composite materials, greater wear than amalgam is apparent after two years (Sachdeo *et al.*, 2004)

Composites: Clinical Issues

- A 5-year comparative prospective study showed a higher incidence of secondary caries in Class 2 composite restorations than in Class 2 amalgam restorations (Mjör *et al.*, 1993)
- Composite resin components may contribute to plaque formation (Kawai and Tsuchitani, 2000)

Composites: Clinical Issues

- The levels of cariogenic bacteria at the margins of composite restorations have been shown to be higher than at those of amalgam restorations (Svanberg *et al.* 1990)

Glass Ionomers: Clinical Issues

- In spite of the fluoride release which occurs from glass ionomer restorations, studies have shown that the leading cause of failure of glass-ionomer restorations is secondary caries (Wilson *et al.*, 1997)
- “no preventive effect was exerted in vivo from the glass-ionomer to protect the adjacent enamel wall from secondary caries attack.” (Papagiannoulis *et al.*, 2002)

Composites: Biological Risks

- Estrogenicity issue—debate ongoing
- Cytotoxicity and other effects
- Allergenicity—patients slightly more likely to be allergic to one or more resin composite ingredients (8%), than to mercury (6%)
(Vamnes *et al.*, 2004)
- Blue light—“dental photocuring lights pose at least some risk to oral cells” (Wataha *et al.*, 2004)

