

Introduction of samples into ICP

Samples

- **Liquid (wet or dry aerosol)**
- **Solid (dry aerosol, direct solids vaporization)**
- **Gaseous (volatile compounds and gases)**

Requirements for an aerosol properties

- **Efficient generating of aerosols independent of sample properties**
- **Good efficiency of an aerosol transport**
- **Minimum memory effects**
- **Stability of an aerosol generating and transport**
- **Identical composition of a sample and aerosol**
- **Dominant yield of fine particles (μm)**

Liquid sample introduction

1) Nebulization of solutions

a) Pneumatic nebulization (Gouy 1879)

- **Capillary nebulizers - with/without suction**

- ☞ **Concentric nebulizer - with aspirating effect**
(Meinhard 1977)

- ☞ **Cross-flow nebulizer - with/without suction**
(Kniseley 1974, Boumans 1982)

- **Babington-type nebulizers - no suction effect**
(Babington 1973)

- ☞ **V-groove nebulizer** (Wolcott & Sobel 1978)

- ☞ **Grid nebulizer** (Hildebrand)

- ☞ **Fritted disc nebulizer** (Apel & Bienewski 1977)

Liquid sample introduction

1) Nebulization of solutions (continued)

b) Nebulization independent of a carrier gas flow

- ☞ **Jet-impact nebulizer** (Doherty & Hieftje 1984)
- ☞ **Hydraulic high pressure nebulizer** (Knauer)
- ☞ **Thermospray**
- ☞ **Ultrasonic nebulizer** (Dunken & Pforr 1963)

2) Electrothermal vaporization (ETV)

a) Electrically heated metal vaporizers

- ☞ **Ta filament vaporizer** - resistance heating (Nixon, Fassel & Kniseley 1974)
- ☞ **Tungsten loop** - cathode of μ -arc (Keilsohn, Deutsch & Hieftje 1983)

Liquid sample introduction

2) Electrothermal vaporization (continued)

b) Electrically heated graphite vaporizers

☞ Graphite rod (Gunn, Millard Kirkbright 1978)

☞ Graphite cup (Ng & Caruso 1982)

☞ Graphite furnace (Aziz, Broekaert & Leis 1982)

3) Direct sample insertion devices

Samples inserted axially (in injector position) into ICP -
induction and contact heating

☞ Graphite electrode (Salin & Horlick 1979)

☞ Graphite crucible (Sommer & Ohls 1980)

Liquid sample introduction

4) Hyphenated techniques

📄 **Liquid chromatographic techniques** (Van Loon 1979)

📄 **Flow injection techniques** (Greenfield 1981)

Gaseous sample introduction

📄 **Generation of volatile hydride** (As, Sb, Bi, Se, Te, Ge, Sn)
(Thompson, Pahlavanpour, Walton & Kirkbright 1978)

📄 **Volatile β -diketonates of Co, Cr, Fe, Mn, Zn** (Black & Browner 1981), **dithiocarbamates, fluoroacetates**

📄 **Gas chromatographic separation of organic compounds with ICP detection: F, Cl, Br, I, B, C, S, P, O, N.** (Windsor & Bonner Denton 1979)

📄 **Air introduction - purity check** (Trassy)

Solid sample introduction

1) Powdered samples

- ☞ Nebulization of slurries (Mohamed, Brown & Fry 1981)
- ☞ Electrothermal vaporization
- ☞ Fluidized bed (Nimalasiri, de Silva & Guevermont 1986)
- ☞ Direct solid insertion device
- ☞ Laser ablation (Abercrombie, Silvester & Stoute 1977)

2) Compact samples

- ☞ Electric arc erosion (ablation) (Dahlquist 1975)
- ☞ Electric spark erosion (ablation) (Human, Oakes, Scott & West 1976)
- ☞ Laser ablation

Pneumatic nebulization

- **Three main types of liquid breakup:**

- ☞ **dropwise, stringwise, filmwise** - depending on the relative velocity of the gas compared with the liquid.

- ☞ As the relative velocity changes, so does the breakup pattern, quite independently of the liquid nebulized.

- ☞ The transition points for different liquids are within the relative velocity range 5 to 50 m/s. Increases in the relative velocity change the breakup pattern in the order dropwise to stringwise to filmwise.

- ☞ Most liquids breakup in a filmwise manner at a relative velocity above 50 m/s. **For common ICP nebulizers, filmwise breakup is observed.**

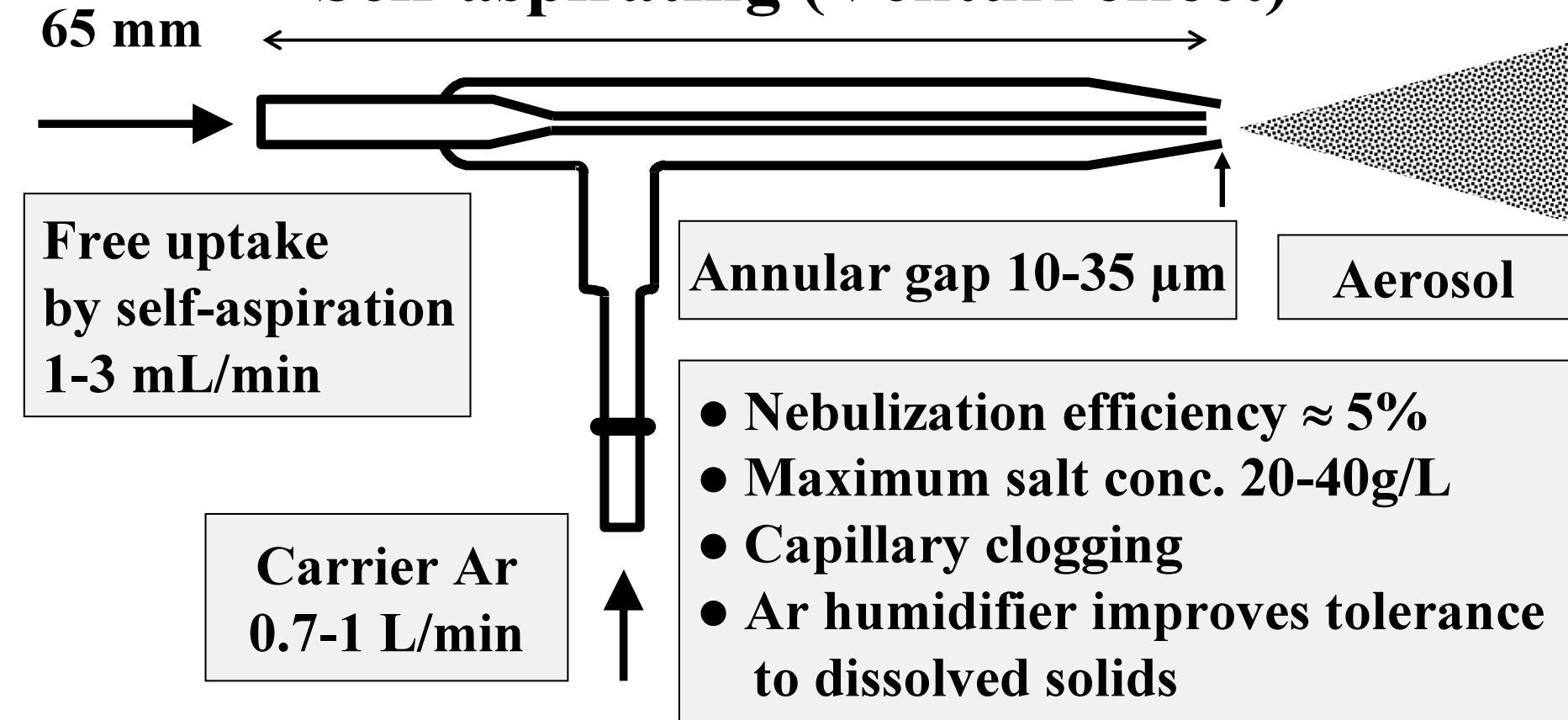
Pneumatic nebulization


- **Dropwise breakup** - this pattern appears at low rel. velocities (gas to liquid) as the result of waves set up in the rodlike liquid jet influenced by the gas flow. The rod develops a number of nodes, and as the nodes grow, the liquid jet breaks up into drops. The thin drawn-out portions between the drops form one to three small droplets.
- **Stringwise breakup** - at higher velocity the liquid stream begins to flutter, as it is exposed to a strong “wind” and the nodes are shattered, tailing out into long strings. The nodes form larger droplets while the tails form smaller ones.

Pneumatic nebulization

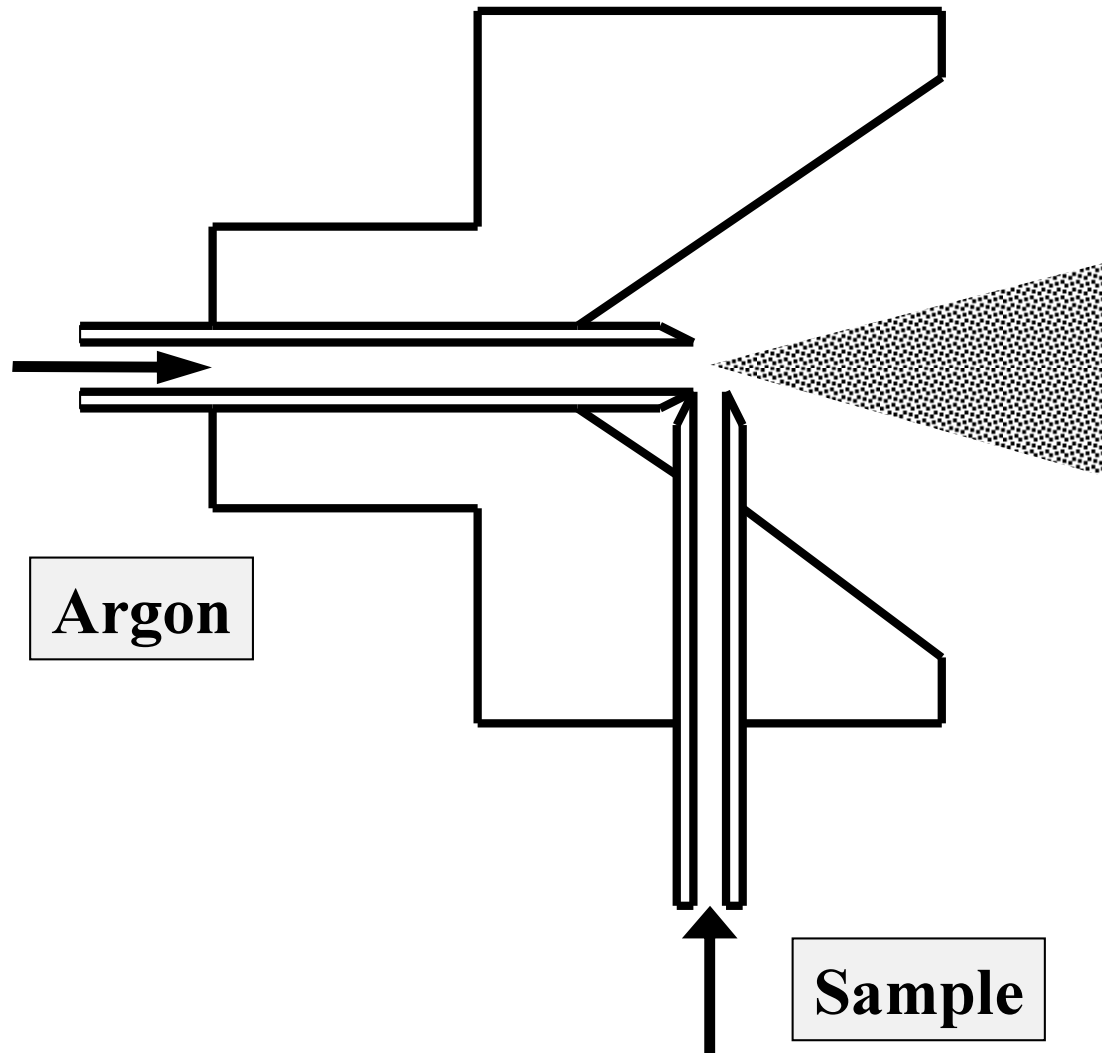
- **Filmwise breakup** - as the relative velocity is increase even further, the gas causes the drops to become flattened and subsequently blown out into the form of a bag or a casting net with a roughly circular rim. The bursting of this bag produces a large number of fine strings and filaments which, in turn, form droplets. The rim, containing the major part of the original volume of the drop, also breaks up, forming larger droplets. If the relative velocity is increased even further, no new pattern develops, but the drops, bags, strings and filament become smaller.

Meinhard Concentric Glass Nebulizer (CGN) Self-aspirating (Venturi effect)



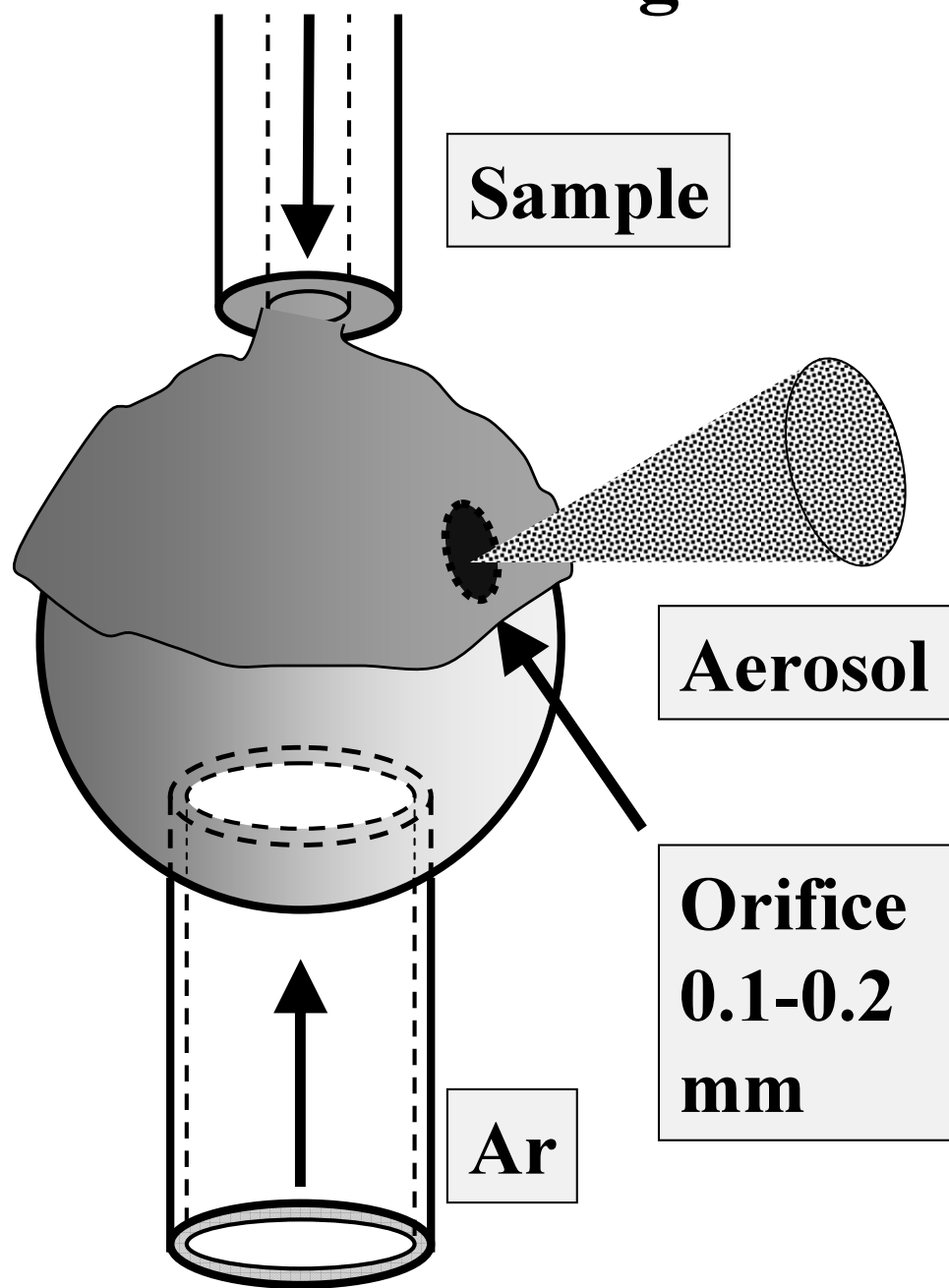
 Pumping eliminates influence of solution properties and level height. "Starving" nebulizer - pump delivers less than suction uptake \Rightarrow good signal stability

Cross-flow nebulizer (CFN) with or without Venturi effect



- Less efficient than CGN
- Less sensitivity
- Larger capillaries
- Less clogging problems
- More rugged
- Corrosion resistant tips of nebulizer (Pt, sapphire)
- Ar flow 0.6-1 L/min
- Solution pumping 1-2 mL/min

Babington nebulizer (1973)

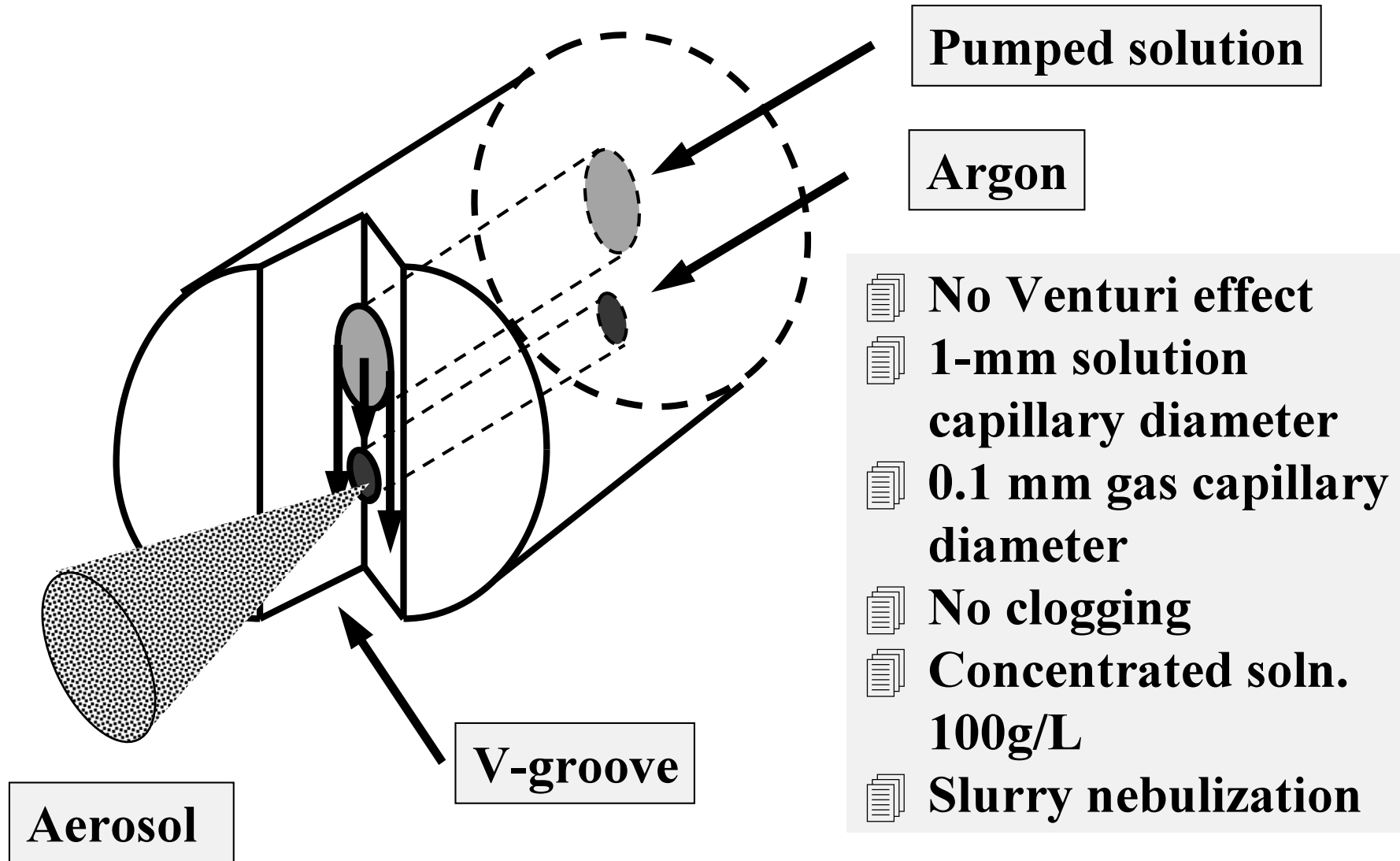


The liquid flows over a smooth surface with small hole in it. High speed Ar gas emanating from the hole shears the sheet of the liquid into small droplets.

- ☞ No Venturi effect
- ☞ Resistant to clogging
- ☞ Nebulize viscose liquids
- ☞ Various modifications

Garbarino & Taylor 1980

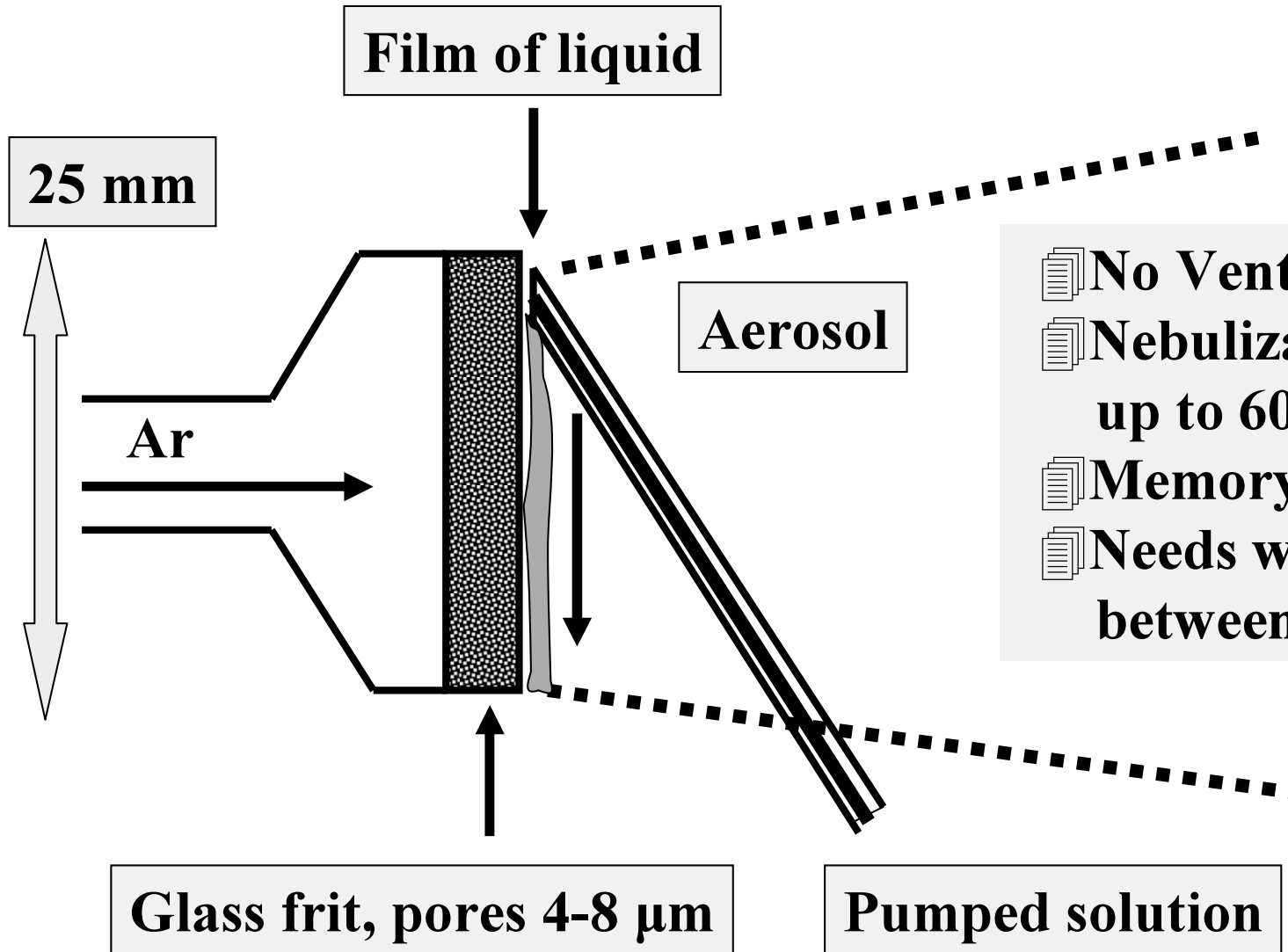
V-groove nebulizer = high solids nebulizer = maximum dissolved solids nebulizer



Wolcott & Sobel 1978

Suddendorf & Boyer 1980

Glass-frit nebulizer



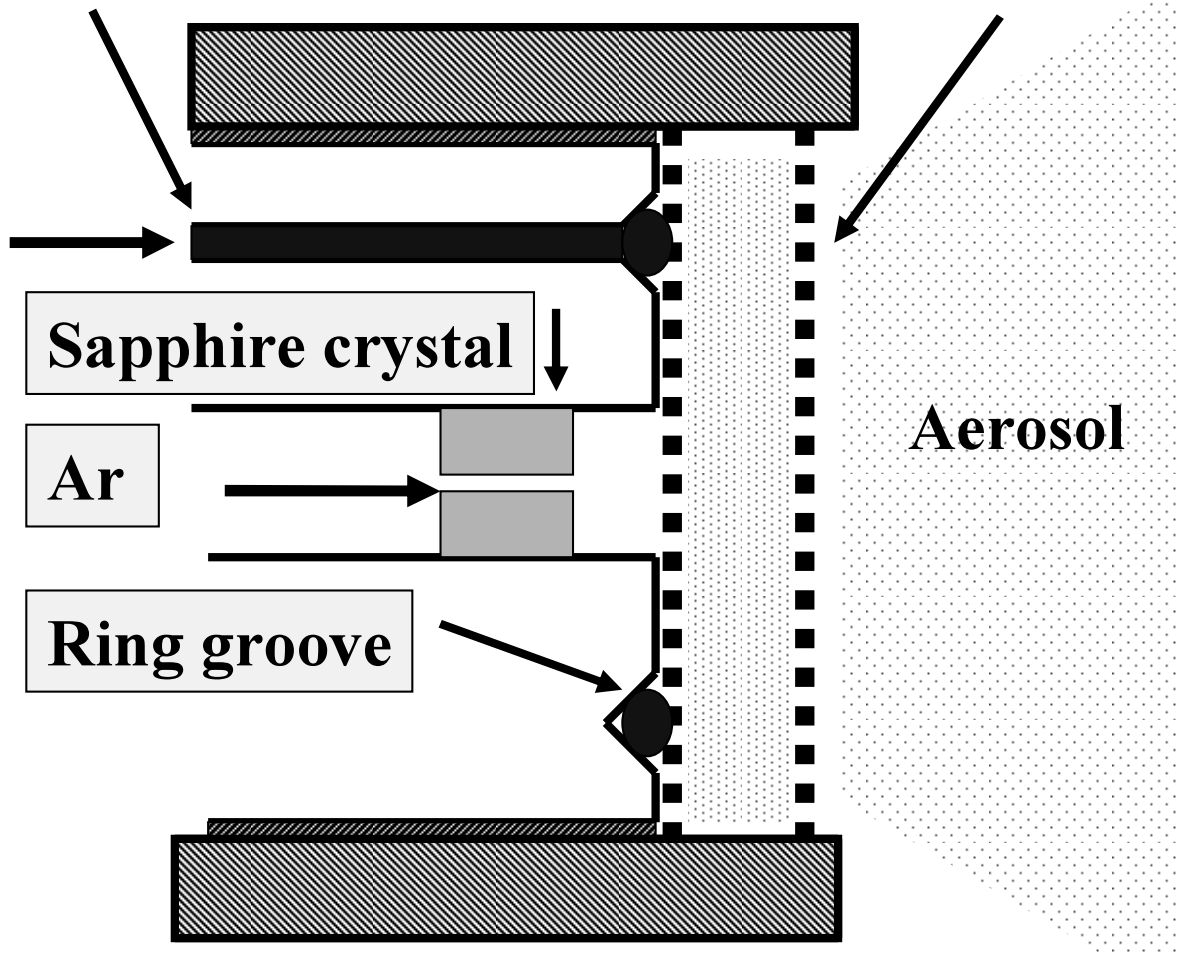
- ☞ No Venturi effect
- ☞ Nebulization efficiency up to 60%
- ☞ Memory effects
- ☞ Needs washing out between samples

Grid nebulizer (Hildebrand)

12 mm

Solution capillary

2 platinum grids



- ☞ No Venturi effect
- ☞ Sapphire jet diam. 0.17 mm
- ☞ Concentrated solutions
- ☞ Viscous solutions
- ☞ Hydride generation

Hagen-Poiseuille equation

$$Q_L = \frac{\pi R^4 \Delta P}{8\eta L}$$

Q_L liquid flow rate
 R capillary radius
 ΔP pressure differential
 η solution viscosity
 L capillary length

Nukiyama-Tanasawa equation

$$d_0 = \frac{585}{v_G (\sigma/\rho)^{1/2}} + 597 \left[\frac{\eta}{(\sigma\rho)^{1/2}} \right]^{0.45} \left(\frac{1000 Q_L}{Q_G} \right)^{3/2}$$

d_0 - mean Sauter droplet diameter (μm), v_G - difference between gas and liquid velocity (m/s), ρ - density of liquid (g/cm^3), η - viscosity of liquid (poise), σ - surface tension (dyne/cm), Q_L , Q_G flow rate of liquid and gas (cm^3/s)

Pneumatic nebulization

Use of a peristaltic pump with self-aspirating nebulizers is advantageous because:

- ☞ it ensures a stable uptake rate
- ☞ reduces nebulization effects that arise from viscosity differences between samples.

Nebulization effects contribute to matrix effects in ICP spectrometry. Viscosity influences aerosol particle diameter d_0 in Nukiyama-Tanasawa equation:

- ☞ At low gas flow rates ($Q_L/Q_G > 10^{-3}$) the viscosity influences d_0 through Q_L in the 2nd term of this equation via the Hagen-Poiseuille law.
- ☞ Viscosity influences d_0 directly in the 2nd term of N-T

Ultrasonic nebulization (USN)

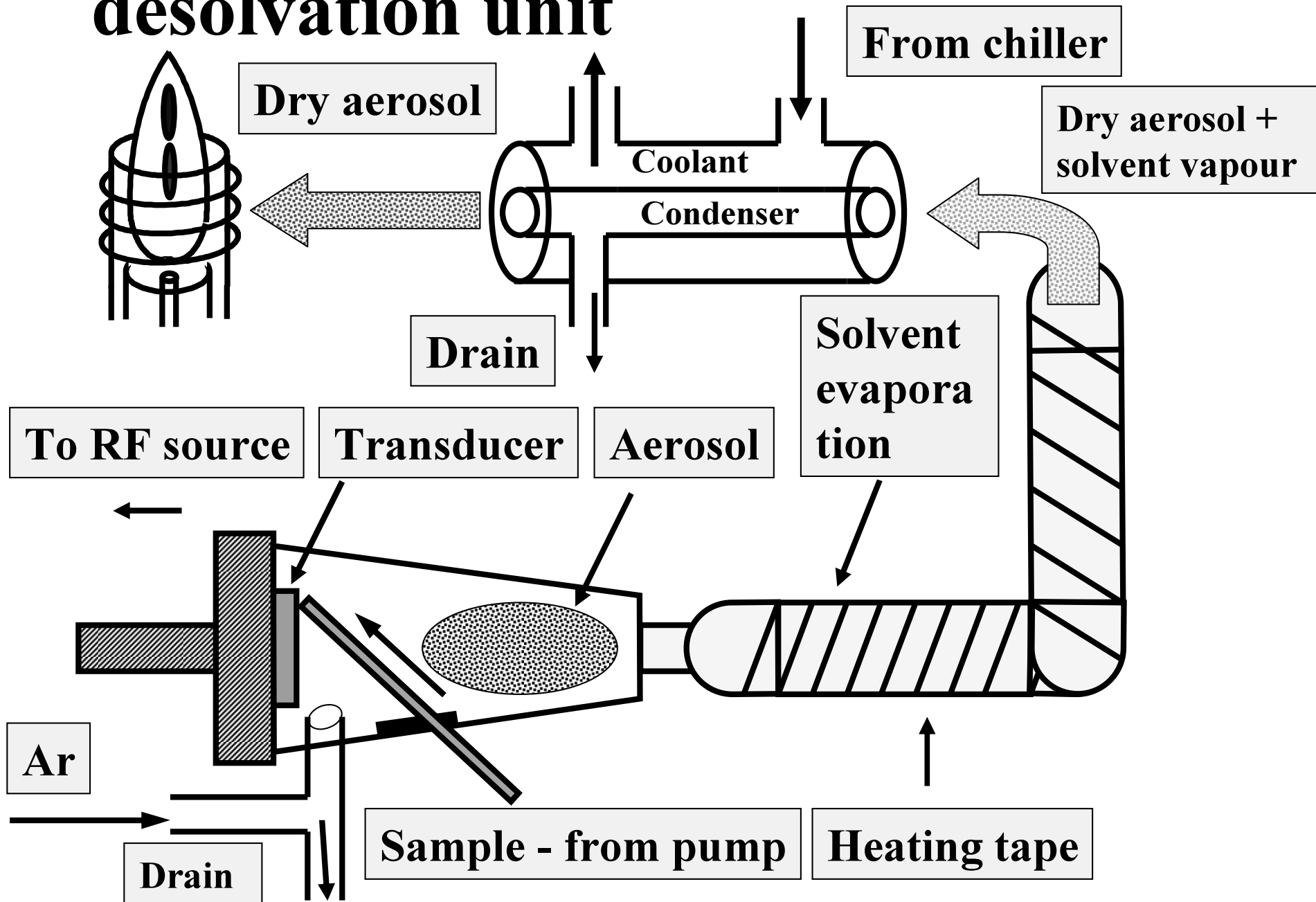
Ultrasonic generator drives a piezoelectric crystal at a frequency between 200 kHz and 10 MHz. A longitudinal acoustic wave is produced by an oscillator coupled to a transducer. The wave propagates perpendicularly from the crystal surface towards the liquid-gas interface and produces a pressure that breaks the surface into an aerosol. The wavelength of the surface wave is given by the relation:

$$\lambda = \left(\frac{8\pi \sigma}{\rho f^2} \right)^{1/3}$$

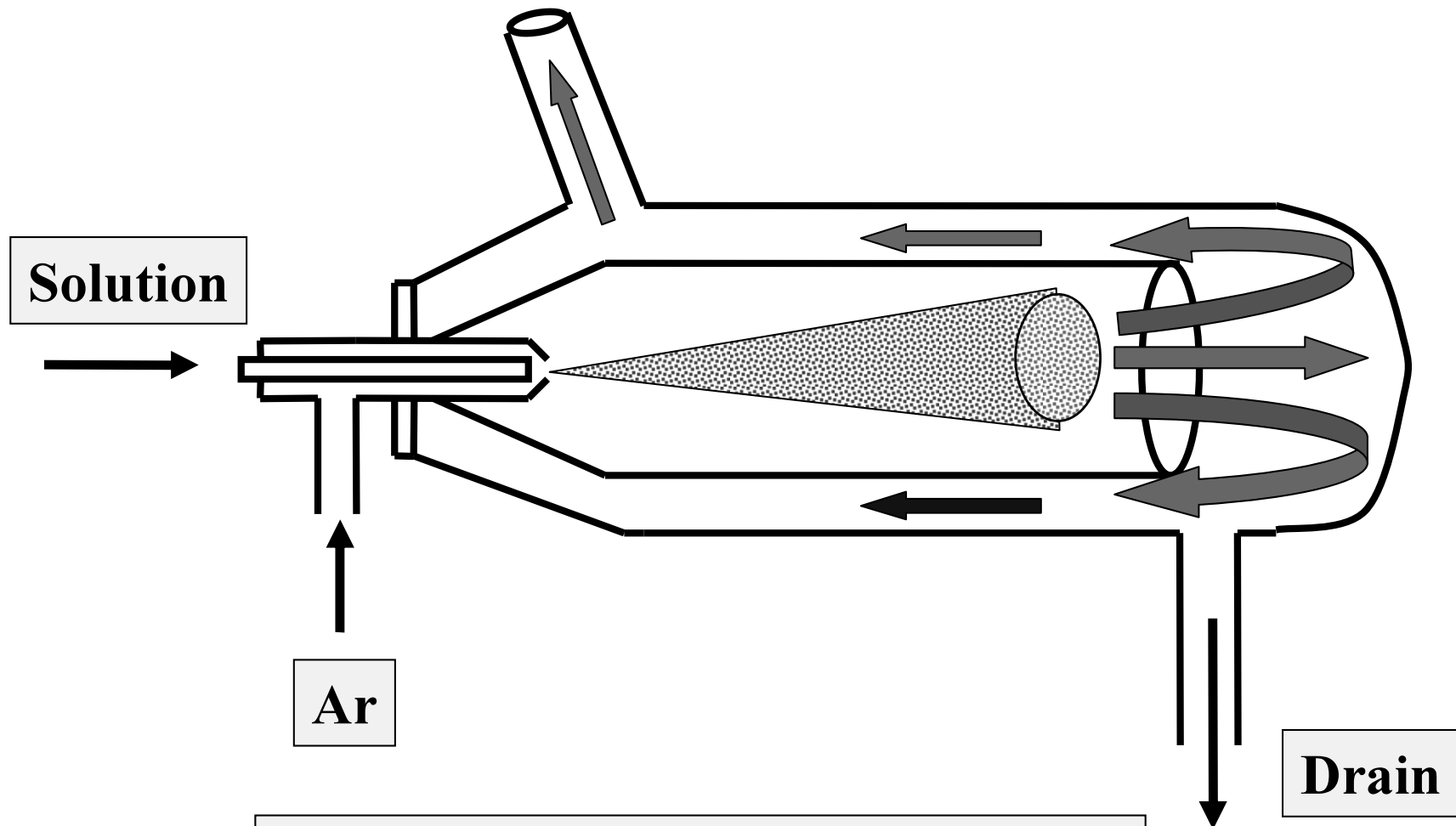
where λ is wavelength, σ is surface tension, ρ is liquid density and f is ultrasonic frequency. The average droplet diameter is then

$$D = 0.34 \lambda$$

Ultrasonic nebulizer (USN) with desolvation unit



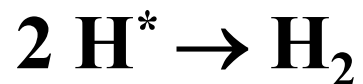
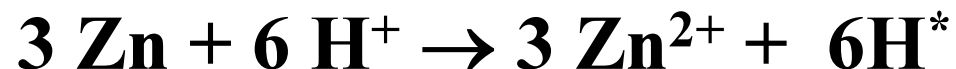
Scott double-pass spray chamber



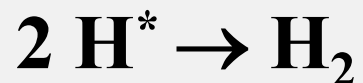
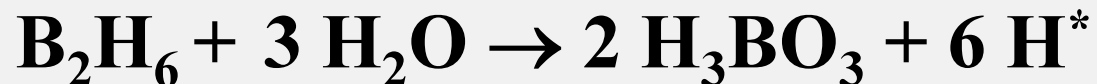
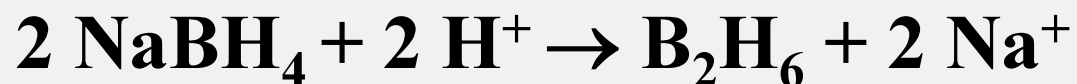
Scott, Fassel, Kniseley Nixon (1974)

Hydride generation (HG-ICP)

Historically - Marsh reaction in Gutzeit test for As



Since 1972:



Hydride generation (HG-ICP)

As, Sb, Bi, Se, Te, Ge, Sn, Pb

- High efficiency with which hydrides are generated and released into the plasma (100%) as compared to the efficiency of pneumatic nebulization (1-5%)
⇒ 10^2 times lower detection limits
- Phase separation from sample matrix ⇒ minimization of spectral interferences resulting from liquid phase
- ⌚ Spectral interferences by CO_2
- Continuous generation - steady state signal, simple arrangement
- Batch generation - transient signal, lower detection limits than continuous systems

Hydride generation (HG-ICP)

- ⌚ **Hydrogen represents an excessive load of the plasma**
- **The batch system makes it possible to get rid of hydrogen by trapping / freezing out of hydrides with subsequent releasing into ICP**
- ⌚ **Chemical interferences are due to transition metals Cu, Ni, Co, Fe, Hg, Cr, Zn, Ti :**
 - 📄 **decrease of reduction efficiency by competitive reactions**
 - 📄 **some ions are reduced to elementary metals with a high active surface which hampers the transfer of hydrides into the gaseous phase**
- **Masking (oxalic acid, EDTA, phenanthroline)**
- **Prereduction of As^{V} to As^{III} and Sb^{V} to Sb^{III} by KI**