Alternative Sample Introduction Systems

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The secret of being a bore is to tell everything.

Voltaire, (Francois Marie Arouet), 1694-1778

You will have to talk for an hour and 15 minutes.

Yngvar Thommasen

What does it require to be “an alternative sample introduction technique for ICPs”?

- Convert sample to gas or small aerosol particles (dry or “wet”)
  - Reproducible transport to ICP
    - **IDEAL**: 100% efficient, independent of matrix
  - Limited tolerance by ICP of “mass” of material delivered
  - Limited tolerance by ICP of type and amount of molecular gases delivered

What won’t be discussed…

- Nebulizers (of all forms)
- Laser ablation
- Sputtering (e.g., glow discharge)

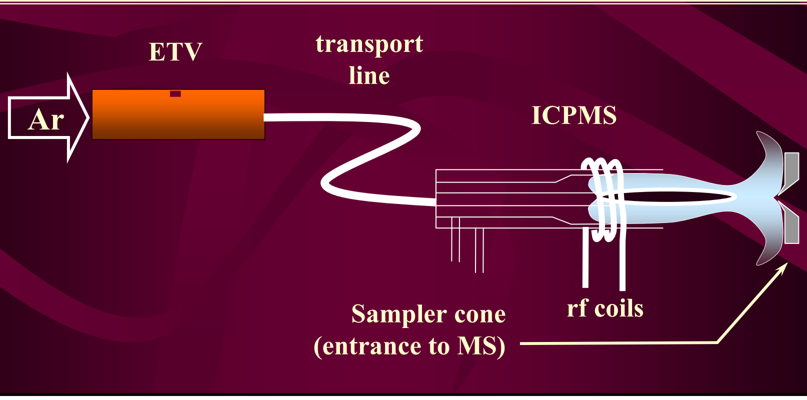
What will be discussed…

- Electrothermal vaporizers (ETV)
- Slurry sampling with ETV
- Gaseous metal production (e.g., hydrides)

Knowledge of ETA (and GFAA) will probably help you. It certainly will not “hurt” you…

but it may lead you down a longer path than you need to take to reach your objective if you forget that ...

ETV ≠ ETA



ETV

transport line

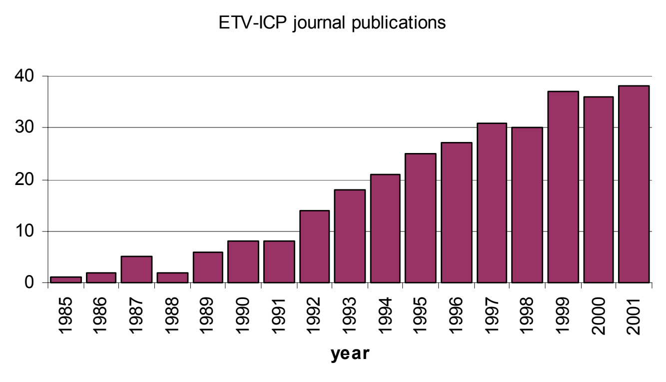
Ar

ICPMS

rf coils

Sampler cone (entrance to MS)

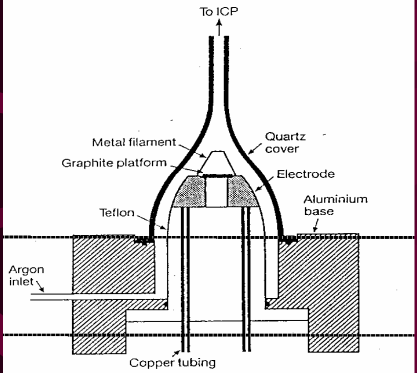
ETV use for sample introduction into an ICP



Instrumentation

- Different configurations
  - Directly heated filament or platform-type
  - Tube type (>75% of the ETV systems)
    - “End-on streaming” *(most common configuration)*
    - “Upward streaming”
  - Misc.
    - Insertion of metal wire loop in tube type
    - Electrically heated wire loop in torch (insertion probes)
- Substrates used
  - Re, W, Ta, Mo, variety of graphites (ranging from pyrolytically-coated electrographite to glassy carbon)

First platform or filament-type device used for ETV-ICPMS system



First type of ETV for ICPMS [2]

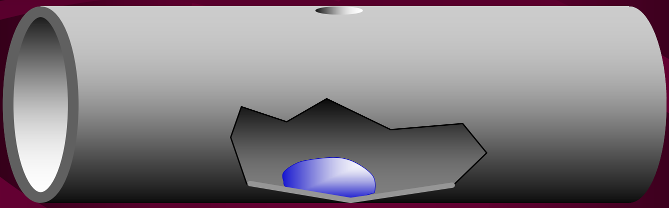
- Kirkbright et. al.[1] first used ETV for sample introduction in ICPAES
- Argon gas(1L/min) was introduced tangentially to the platform support base
- The effective volume above vaporization surface ~5 mL

[1] Gunn, A.; Millard, D.; Kirkbright, G. *Analyst* (1978) 103, 1066.

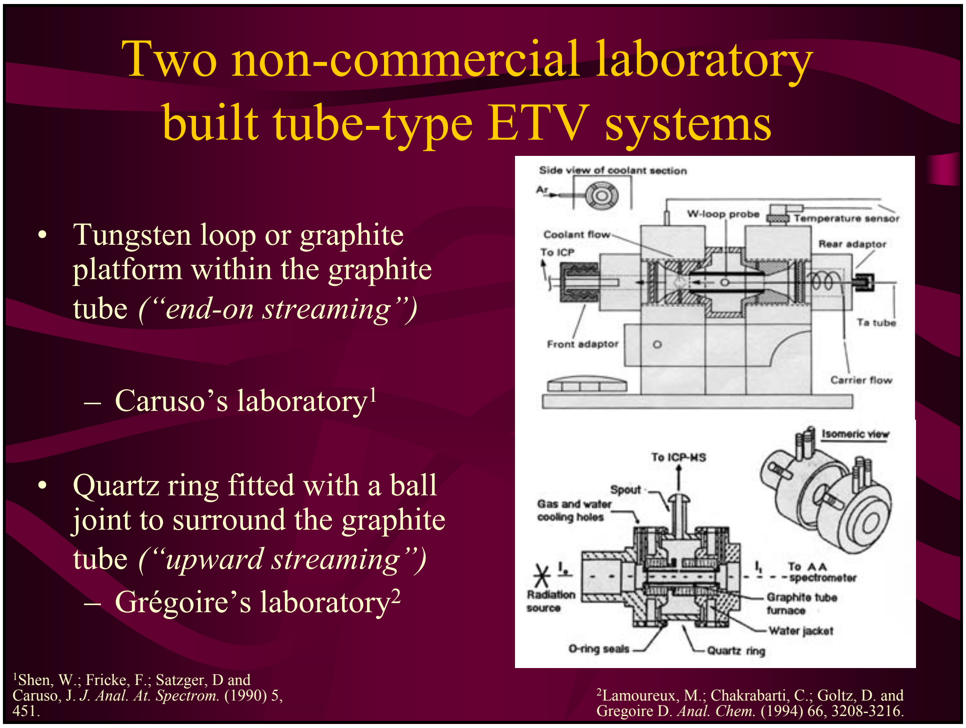
[2] Park, C. J.; Hall, G. E. M. *Pap. - Geol. Surv. Can.* (1986), **86**, 767-73.

Common graphite tube-type ETV is modification of “graphite furnace atomizer” used in GFAAS (aka “ETAAS”)

Pyrolytic-coated electrographite
Used with and without “platform” *



* Platform may serve no useful purpose for ETV introduction but may minimize use for refractory elements.

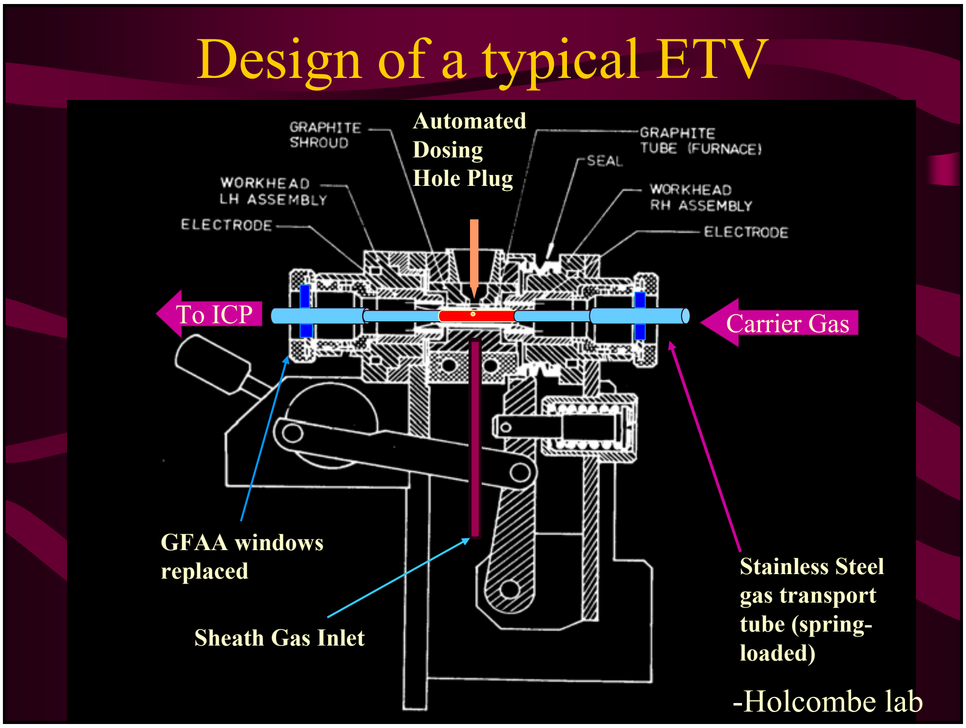


Two non-commercial laboratory built tube-type ETV systems

- Tungsten loop or graphite platform within the graphite tube *("end-on streaming")*
  - Caruso's laboratory[1]
- Quartz ring fitted with a ball joint to surround the graphite tube *("upward streaming")*
  - Grégoire's laboratory[2]

[1] Shen, W.; Fricke, F.; Satzger, D and Caruso, J. *J. Anal. At. Spectrom.* (1990) 5, 451.

[2] Lamoureux, M.; Chakrabarti, C.; Goltz, D. and Gregoire D. *Anal. Chem.* (1994) 66, 3208-3216.



Design of a typical ETV

Automated Dosing Hole Plug

To ICP

Carrier Gas

GFAA windows replaced

Sheath Gas Inlet

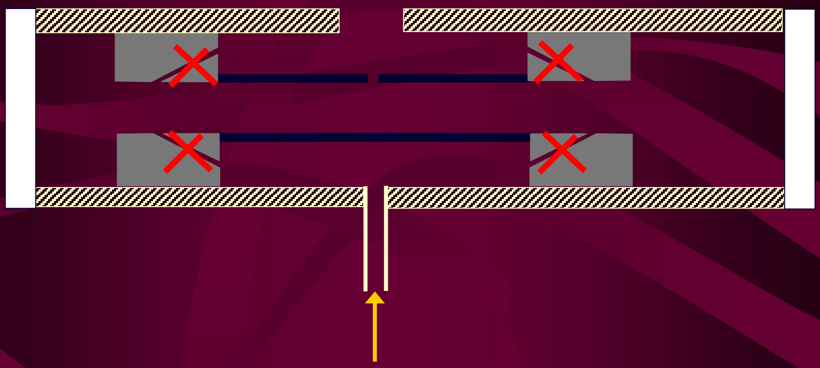
Stainless Steel gas transport tube (spring-loaded)

-Holcombe lab

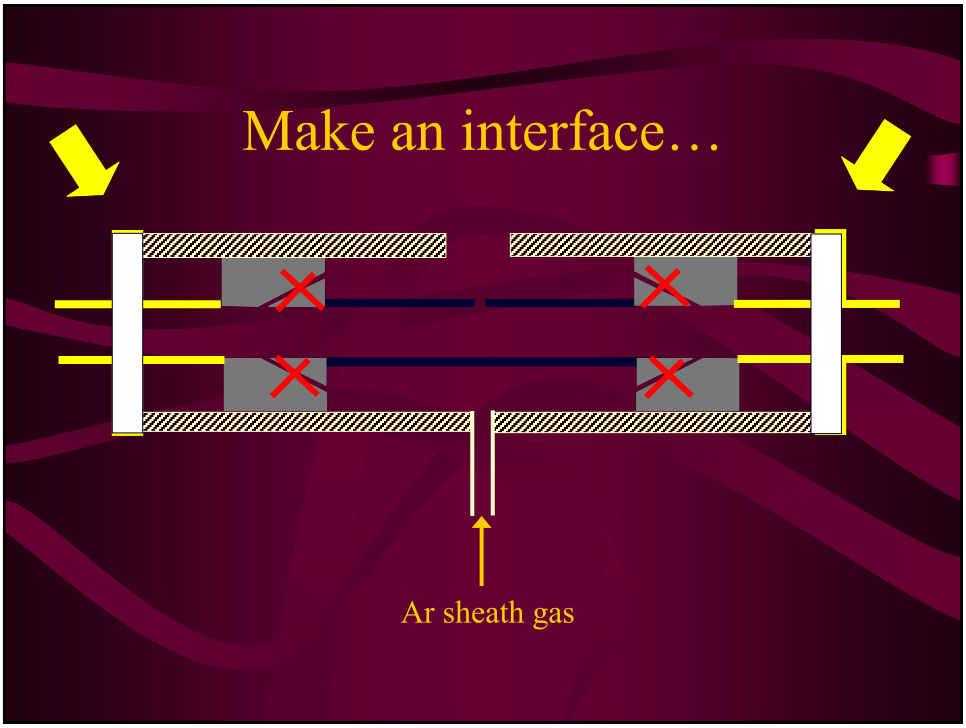
How to put an old graphite furnace into commission as an ETV…

- Plug some holes
- Make an *end cone-to-tubing* interface
- Make a dosing hole plug
- Get the ETV talking to ICP instrument for data collection synchronization (*optional*)

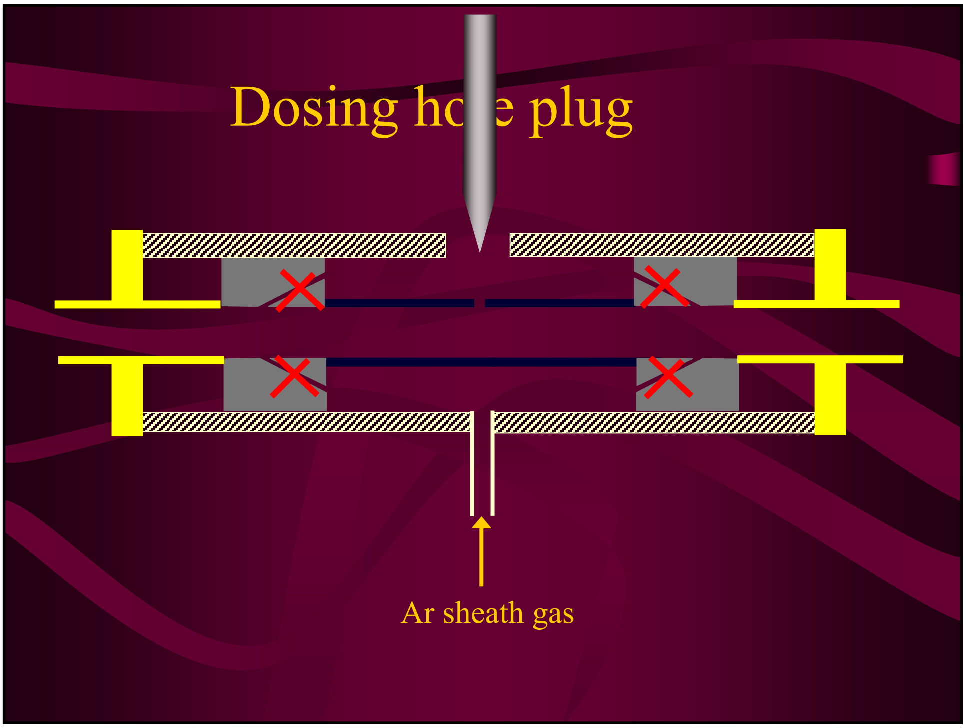
Plug some holes…



Ar sheath gas

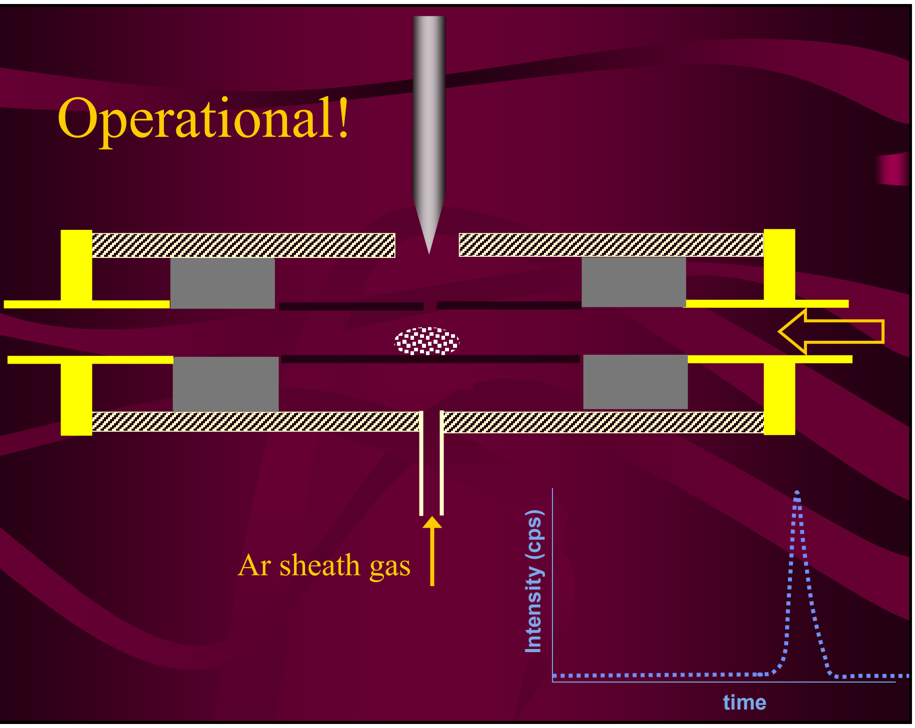


Make an interface…



Dosing hole plug

Operational!



Communication:
ETV ⟷ ICP

(optional)

- ETV should trigger data collection

… or …

- ICP should trigger start of ETV heating cycle

May need to get into timing circuitry of instruments. Sometimes “easy triggers” are available on instrument, e.g., “pen drop”, “aux gas”, “ext. trigger”, etc. *(Mfg. may be of assistance.)*

"Is this ETV just a lot of magic?"

How to use ETV…

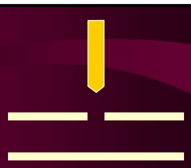
… a walk through the heating program

Sample deposition

- Solutions, aerosols, vapors, slurries can all be used
- Solutions are most common
  - 0-50 µL is typical for tube design
  - Manual pipetting (±5% for skilled operator)
  - Autosampler (<±2% for >10 µL)
  - Use of organic solvents: Spreading can be a problem (CAUTION: analyte loss may occur if organometallics present)

Drying step

(desolvation)



- Gentle dry to avoid splatter (~100°C for ~30 s)
  - 10-20 s for visible disappearance of drop
    - Look through dosing to watch drop disappear
    - *Alternatively*: May be able to use ICPMS and ArH$^+$ or ArO$^+$ to monitory H_2O loss
  - 30-40 s is typical dry time

Gulay pic of ArO thru cycle

Char, Ash, Thermal Pretreatment

- Char:
  - Pyroloysis step in “inert gas” environment (e.g., Ar).
  - Used to remove additional adsorbed water and some matrix components.
  - Also serves to decompose many of the oxyanion salts (e.g., NO_3, SO_4, etc. to the metal oxides).
  - Use and temperature setting not as critical as ETAAS
- Ash:
  - Use of combustion gas (e.g., O_2) to oxidize (“ash”) sample
  - $T_{ash} \leq 900^oC$ to avoid graphite furnace damage
  - Especially useful for biological samples and some organics (NOTE: volatile organics may vaporize before combustion reactions occurs)
- Thermal Pretreatment:
  - Generic term to describe some type of heating after dry step and before vaporization step

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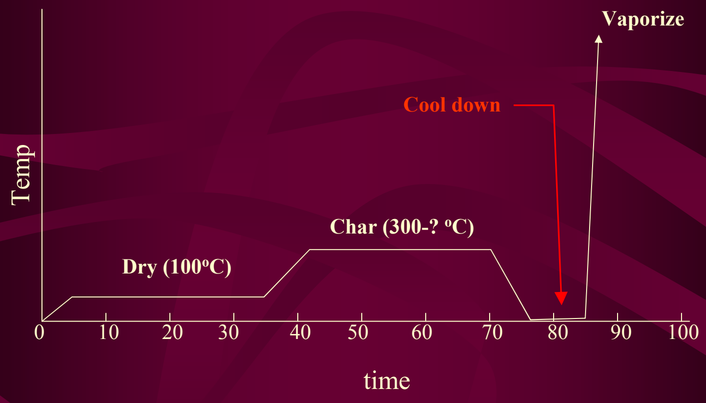
Notes on use of Char step

- Not as critical as in ETAAS
  - In the end we only need to get analyte out of the furnace, and we don’t care what form it is in!
- No need to make “Char curves”
- With volatiles as analytes (e.g., Cd, Zn, Tl…)
  - 200-300°C --removes additional adsorbed water (Not all is removed until T>1000°C!)
- Without volatiles as analytes
  - 200-300°C will likely still be adequate
  - However, you can raise the char to suit needs (e.g., remove matrix, decompose salts, remove more water)
    - $M(NO_3)_{2(s)} \xrightarrow{\sim 200-600^o C} MO_{(s)} + NO_{2(g)} + \frac{1}{2}O_{2(g)}$
  - Generally use 2-5 s ramp to final temperature with total time of ~30 s.

Char



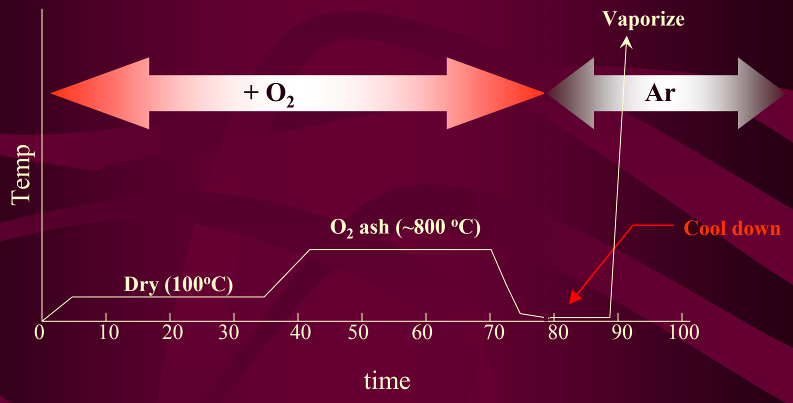
Notes on use of Ash step

- 1-20 % O_2 … or air… can be used during dry also
- Useful for combustion of biological materials and some organics
  - Most biologicals combust ~800ºC (*dull red in color*)
  - Significant oxidation of graphite at T>~1200ºC

$$C_{(s)} + O_2 \xrightarrow{\sim 600^o\,C} CO_{x(ads)} \xrightarrow{\sim 1{,}200^o\,C} CO_{2(g)} + CO_{(g)}$$

- Volatiles (e.g., Cd, Zn, Tl, Pb…) NOT lost *with proper use* of oxygen ashing!

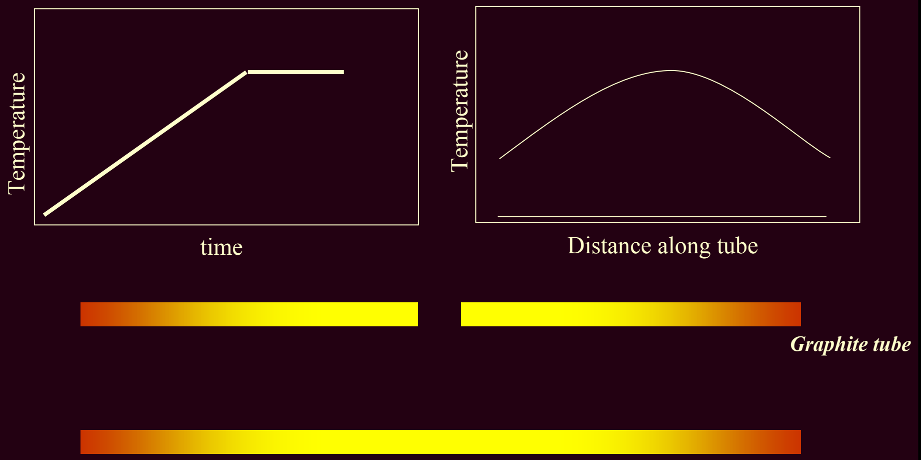
Ashing



Vaporization

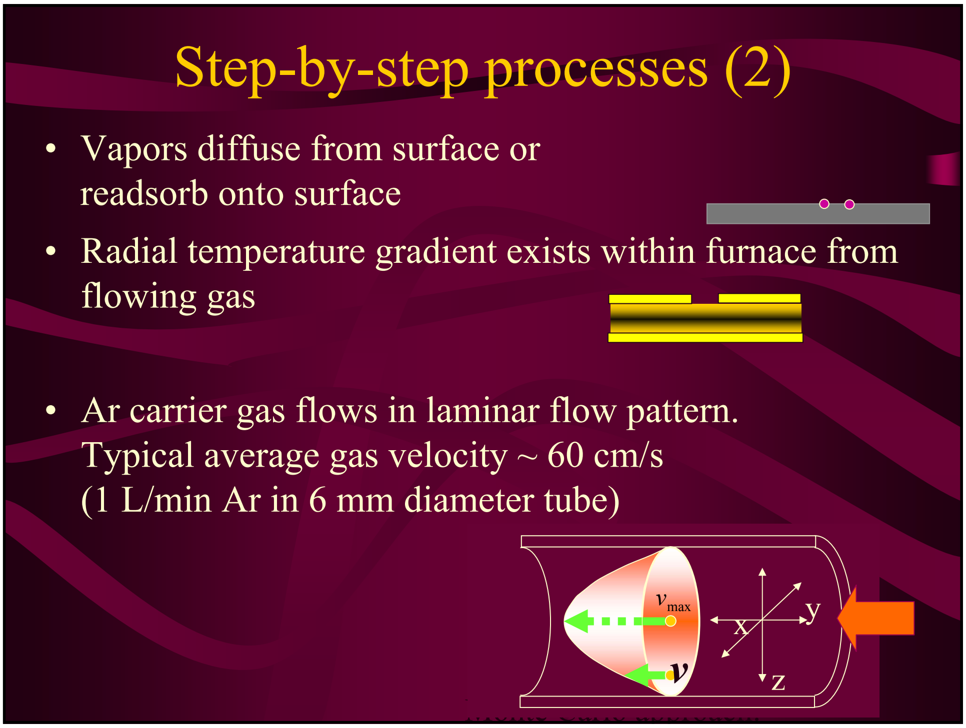
- Final temperature governed by most refractory element determined
  - T_{final} is generally lower than GFAA T_{atomiz}
  - "Memory effects" can be used to determine if vaporization temperature is sufficient
- Why was temperature dropped before vaporization cycle when either "char" or "ash" was used?

Thermal pattern of axially heated tube



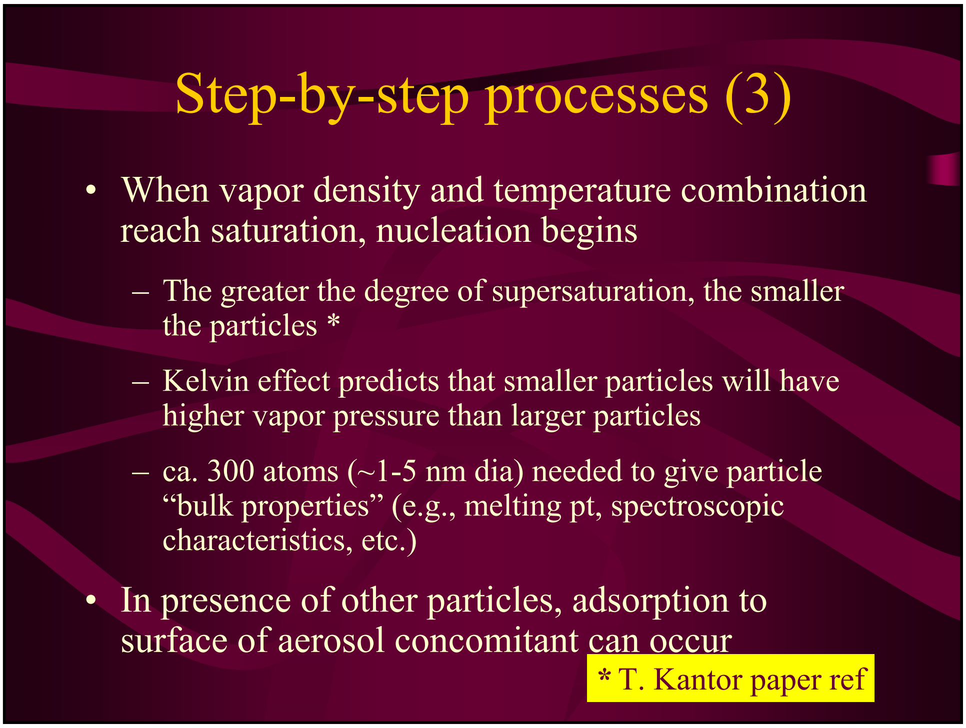
Step-by-step processes (1)

- Heating begins…
  - salts decompose
  - adsorbed water and gases begin to leave graphite
  - reduction of some metal oxides occurs
  - vaporization of metals and other oxides and salts occurs



Step-by-step processes (2)

- Vapors diffuse from surface or readsorb onto surface
- Radial temperature gradient exists within furnace from flowing gas
- Ar carrier gas flows in laminar flow pattern. Typical average gas velocity ~ 60 cm/s (1 L/min Ar in 6 mm diameter tube)



Step-by-step processes (3)

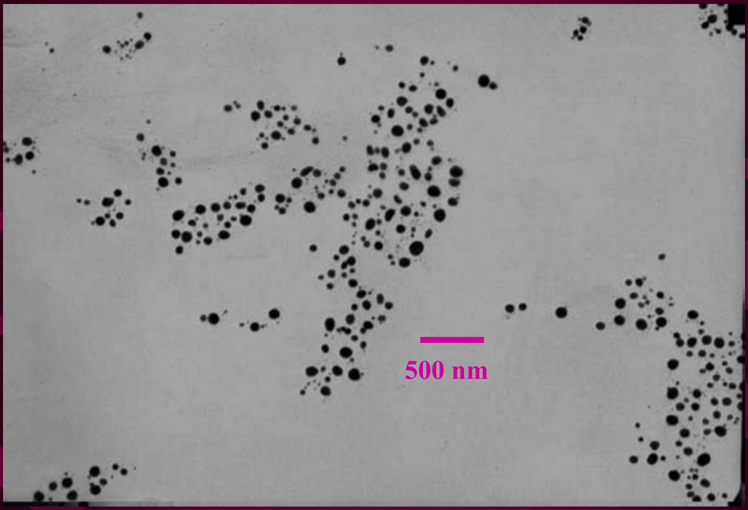
- When vapor density and temperature combination reach saturation, nucleation begins
  - The greater the degree of supersaturation, the smaller the particles *
  - Kelvin effect predicts that smaller particles will have higher vapor pressure than larger particles
  - ca. 300 atoms (~1-5 nm dia) needed to give particle “bulk properties” (e.g., melting pt, spectroscopic characteristics, etc.)
- In presence of other particles, adsorption to surface of aerosol concomitant can occur

* T. Kantor paper ref

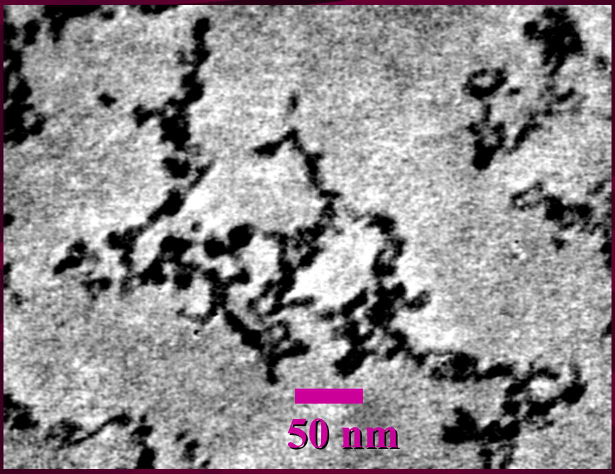
Step-by-step processes (4)

- Within a few cm outside the ETV, gas temperatures are <100°C
- Most analyte species are aerosol particles (Exceptions: Hg, Cd, Zn, Pb, other very volatile metals and oxides)
- Particle sizes are dominated by diameters that are $\leq$ 100 nm; with many <10 nm for dilute samples.

What are we “transporting”?



Ag particles collected thermophoretically – TEM image (100 μg Ag)



Pd

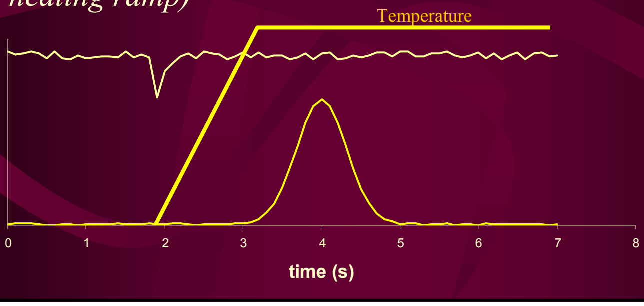
Thermophoretic Collection of 1 µg Pd - TEM Image

Step-by-step processes (5)

- Generation from ETV surface generally complete in <1 s (and *probably <0.2 s!*)
- Aerosol particles start moving down transport tubing (0.3 – 1.5 m long) to ICP
- But… before this takes place, the heating of the furnace generates a pressure pulse that can be detected by the ICP-OES (baseline shift) or ICPMS (dip or spike in Ar_2^+)

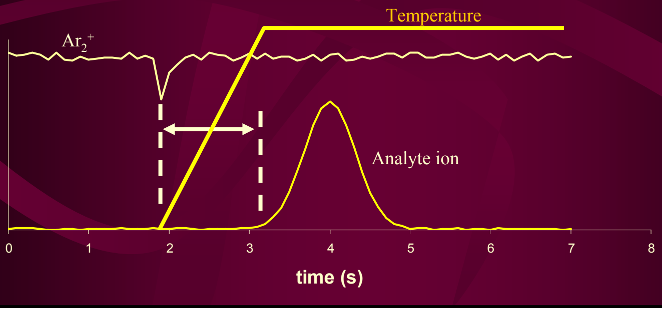
Pressure pulse detected in Ar_2^+

- Pressure pulse comes from increased gas flow in central channel from thermal gas expansion; moves at speed of sound in Ar (FAST!)
- Pressure pulse increases with heating rate and with ΔT/T *(i.e., most severe at start of heating when using a linear heating ramp)*



Step-by-step processes (6)

- Pressure pulse moving at speed of sound in Ar **but** sample aerosol moving at velocity of carrier gas (e.g., ~60 cm/s… or ~2 km/h)
- Thus, time delay exists before signal detected and sample released from ETV
  (1-2 s for ~1 m long transport tube)



Step-by-step processes (7)

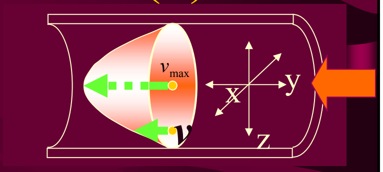
- Transport efficiency:

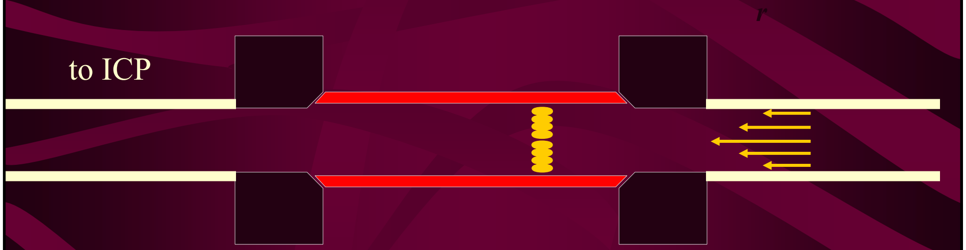
$$\varepsilon = \frac{\text{Mass entering ICP}}{\text{Mass deposited in ETV}}$$

- Efficiencies reported by many and vary from 5-75%.
- For tube end-on streaming design, 25-35% seems to be reasonable value[1,2] (REMEMBER: This is ~10-20 times better than conventional nebulizers!)

Step-by-step processes (8)

- Shape of transient signal from ICP governed by broadening due to laminar flow of aerosol down the transport tube





Generation function (even at 5-10 s ramp of ETV) likely occurs within ~0.2 s !

What are limitations of ETV-ICP?

What are limitations of ETV-ICP? (1)

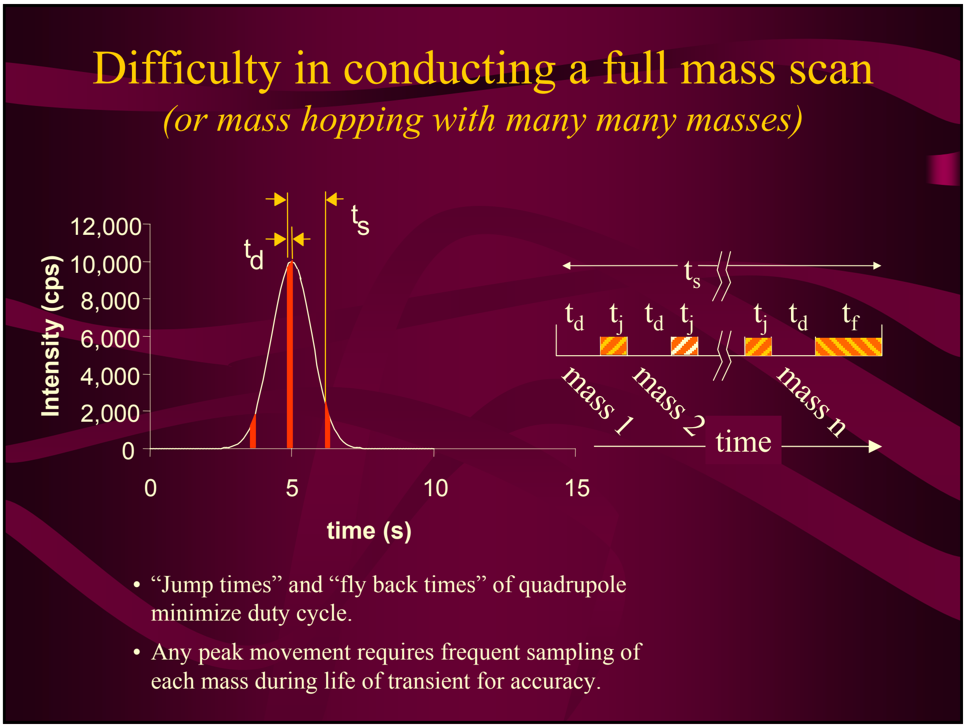
- Sample throughput?
  - 2-3 min per sample (20-30 samples/hour)
    - REMEMBER: No spray chamber clearing required because DRY aerosols are used
- Limits of detection?
  - Depending on type of instrument, 0.5-100 fg is typical (in 10 µL of sample→→ 0.05-10 ppt !)

What are limitations of ETV-ICP? (1)

- Number of masses detectable?
  - ICP(TOF)MS ideally suited for transients like ETV. We can determine EVERY mass with no loss of information (or ion counts) than would be the case for monitoring a single mass!
  - On the more common quadrupole…
    - The profile of the ETV-ICPMS signal is of minimal importance if one can determine the AREA under the signal accurately !

Source of error

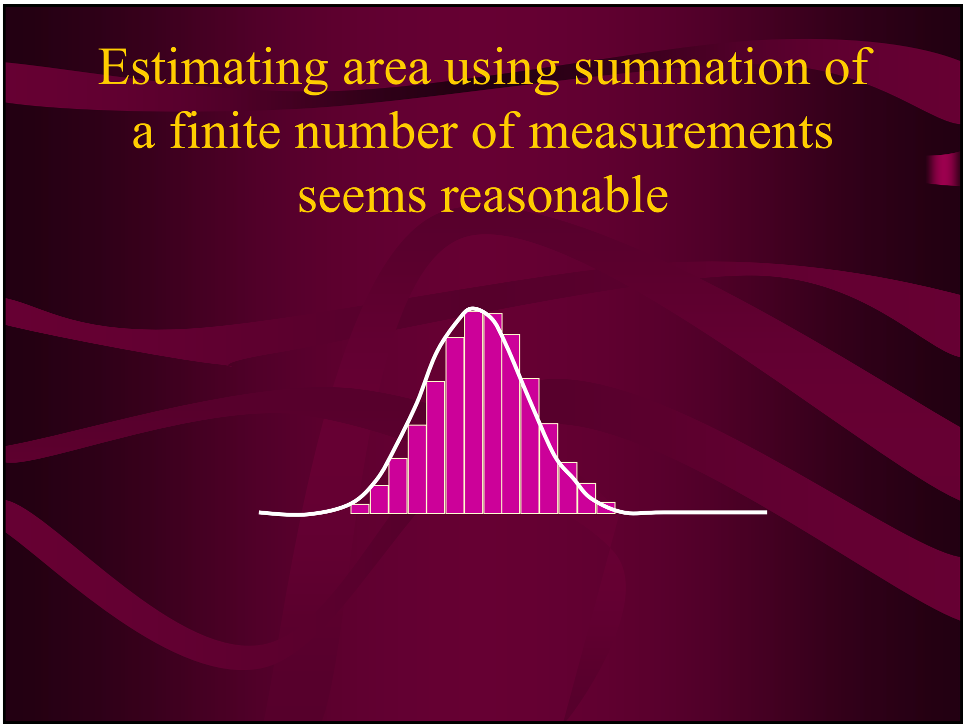
- Sample introduction (sample dosing)
- Statistical counting error (N)
- Peak shifting (relative to data sampling)



Difficulty in conducting a full mass scan

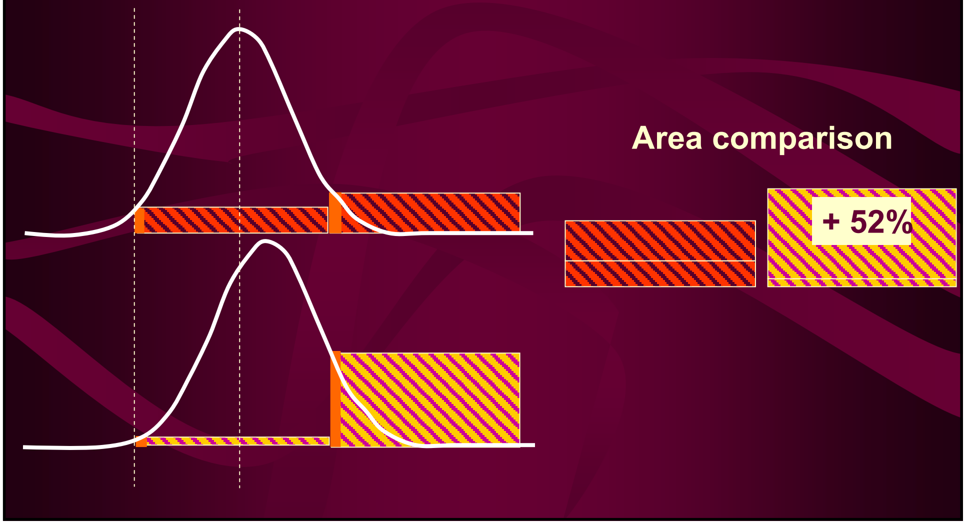
(or mass hopping with many many masses)

- “Jump times” and “fly back times” of quadrupole minimize duty cycle.
- Any peak movement requires frequent sampling of each mass during life of transient for accuracy.



Estimating area using summation of a finite number of measurements seems reasonable

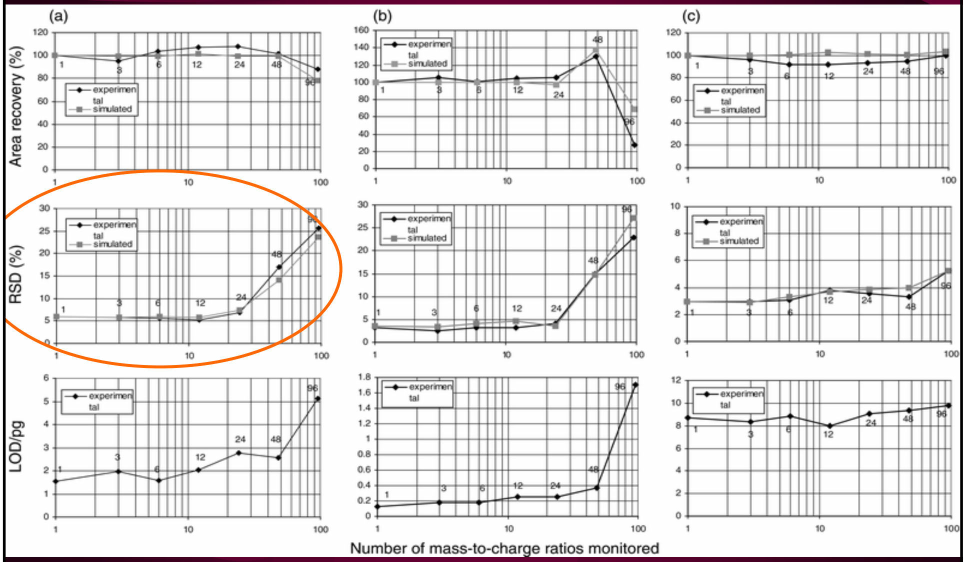
Impact of Peak Shifts on Low Frequency Data Collection



Area comparison

+ 52%

Sensitivity, precision and limits of detection studied as a function of number of m/z monitored for (a) Cd; (b) Co; (c) Ti

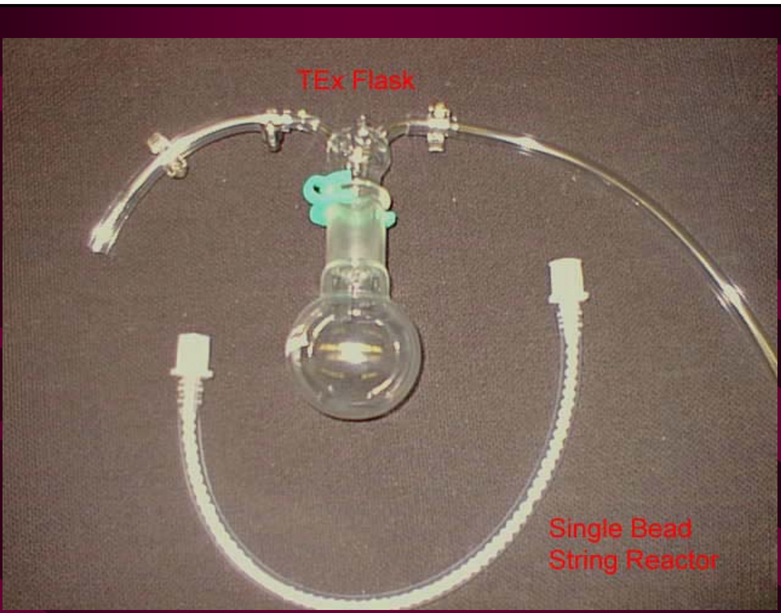


Resano, M.; Verstraete, M.; Vanhaecke, F.; Moens, L.. *J. Anal. Atom. Spectrom.* (2001). **16**, 1018-1027.

Quantitative determination of 21 masses in a single ETV firing with LOQ of 10 ppb

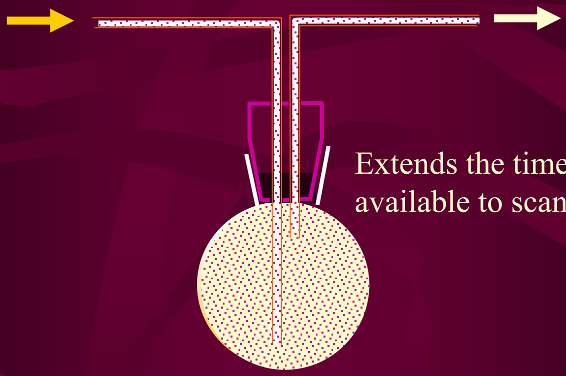
Element	ω^a (s)	ρ^a	s_m (counts/pg)[b]	CLOQ[c] (ppb)	$\%(t_d/t_s)_{min}$[d]	t_s (ms)	t_d (ms)	n_m	% RSD
^{7}Li	0.85	1.1	1690	10	0.03%	250	0.07	**23**	2.3%
^{55}Mn	0.5	1	2330	10	0.02%	250	0.05	**23**	4.9%
^{59}Co	0.7	0.8	2700	10	0.02%	250	0.05	**23**	7.5%
^{63}Cu	0.8	0.8	1390	10	0.04%	250	0.09	**23**	3.5%
^{65}Cu	0.5	1	640	10	0.08%	250	0.19	**23**	5.9%
^{113}In	0.5	0.8	130	10	0.36%	250	0.91	**21**	6.4%
^{115}In	0.45	0.8	2620	10	0.02%	250	0.05	**23**	8.0%
^{121}Sb	0.5	0.7	590	10	0.08%	250	0.21	**23**	6.2%
^{151}Eu	1	0.8	1020	10	0.05%	250	0.12	**23**	2.7%
^{205}Tl	0.5	0.55	690	10	0.07%	250	0.18	**23**	7.4%
^{208}Pb	0.5	1	710	10	0.07%	250	0.17	**23**	3.4%
^{209}Bi	0.6	0.8	1130	10	0.04%	250	0.11	**23**	3.4%

--- sample masses ---



* Moenke-Blankenburg, L.; Gackle, M.; Gunther, D.; Kammel, J. *Processes of laser ablation and vapor transport to the ICP*; Jarvis, K. E., Gray, A. L., Williams, J. G. and Jarvis, I., Ed.; Royal Society of Chemistry: University of Surrey, 1990, pp 1-17

Exponential dilution flask

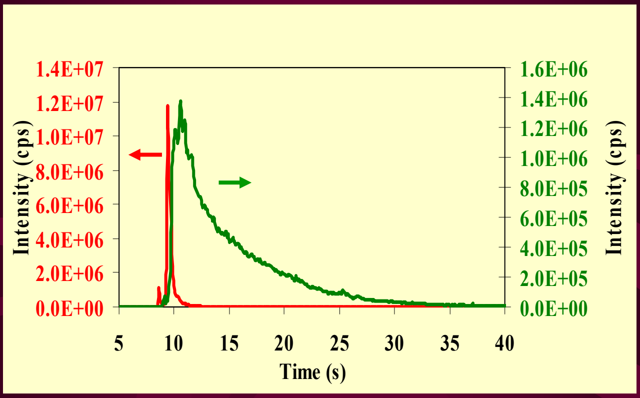


Extends the time
available to scan masses

D. Langer and J. A. Holcombe. *Appl*. *Spec*. 53, **1999**, 1244-1250

TEx flask w/ Texas stuff

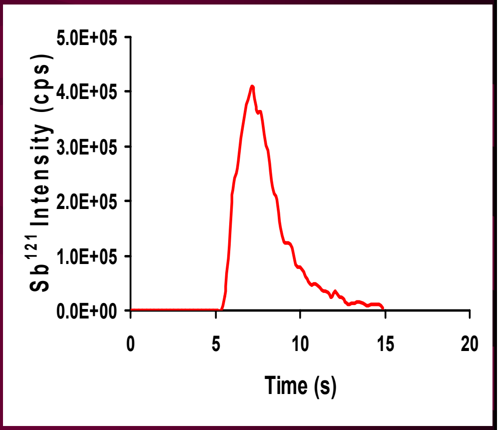
Exponential Signal Extension



- **Exponential dilution allows a full mass scan with a single ETV firing**
- **Normal 1-3 s ETV signals extended up to ca. 20 s**

D. Langer and J. A. Holcombe. *Appl*. *Spec*. 53, **1999**, 1244-1250

Single String Bead Reactor



Gunther et al. *Z. Chem*. 28, **1988**, 227-

What are limitations of ETV-ICP? (3)

- Precision?
  - 2-5% if limited by sample dosing into furnace
  - Near the detection limit: Precision is likely governed by (counting) statistical noise (e.g., S=10 counts yields a S/N~3 or an RSD of ~30% -- for background-free signal measurements)
  - Internal standard generally quite helpful in improving precision.

What are limitations of ETV-ICP? (4)

- Accuracy?
  - Currently, this is matrix dependent and can vary up to ±30% for complex matrices measured against simple aqueous standards
  - REMEMBER: "complex matrices" are those that one would probably *not* be able to use with a nebulizer (e.g., brines, slurries, HLDS)
  - Matrix matching or standard additions can generally improve accuracy to 2-5%

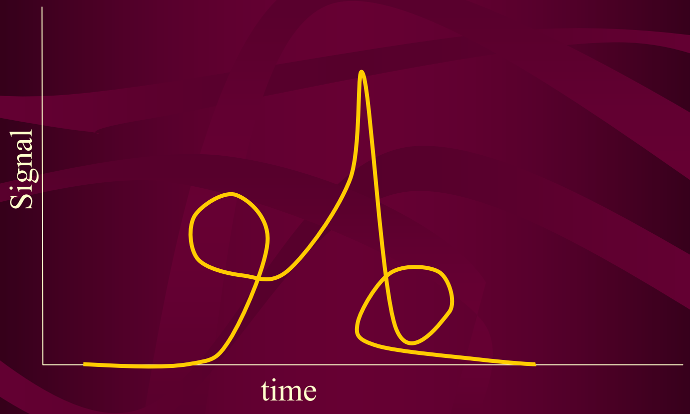
Why use a nebulizer?

- Cost
- Steady state signal to monitor
- Counts can accumulate, so potential for signal averaging, etc. to improve precision and LODs
- Nothing wears out with time
- Easy to understand

How do you collect data… and then what do you do with it?

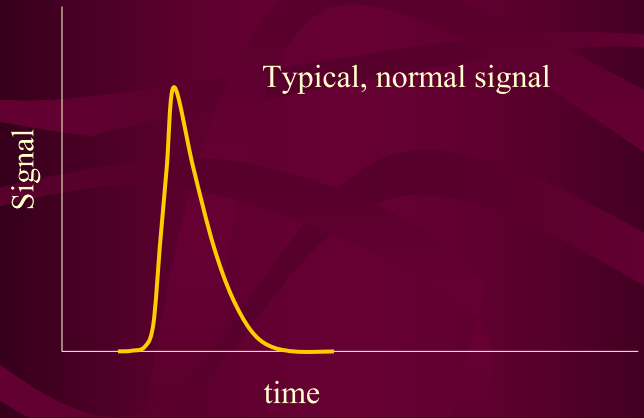
- Most instrument allow **exporting of data** into other program (e.g., Excel®) for data analysis.
- Signal is transient, but you generally *don't need the time resolved signal for quantitative analysis*!
- Tight integration around peak most useful with elevated background levels.
- Having a knowledge of **total counts** can be useful for estimating *limits of detection* (LOD) when LODs are governed by counting statistics.

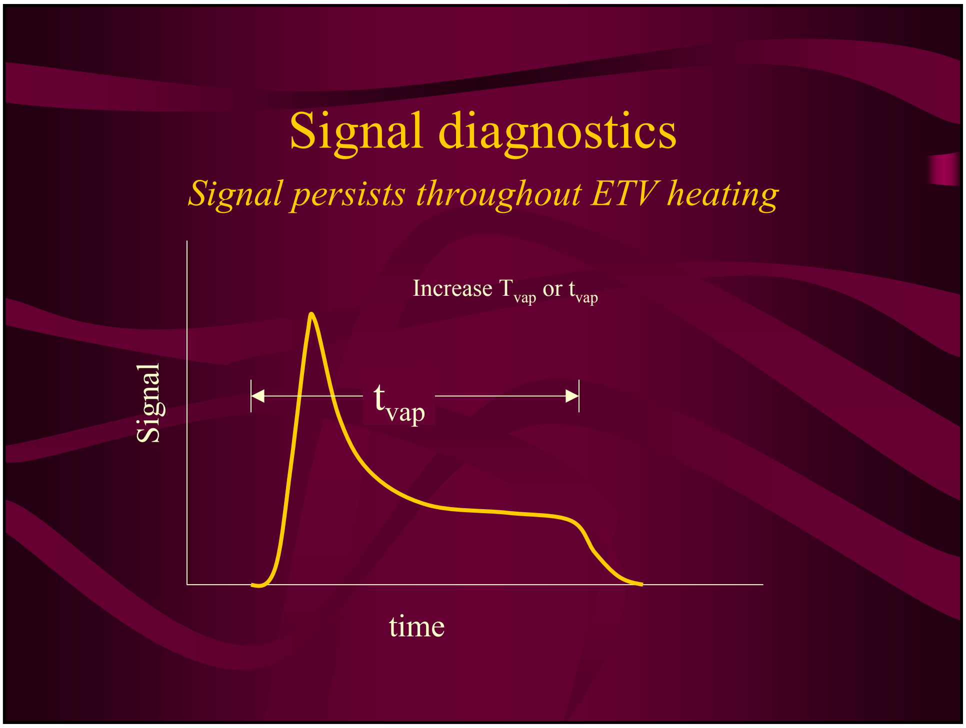
Signal shape can be a useful diagnostic tool



Let's play a game…

Signal diagnostics

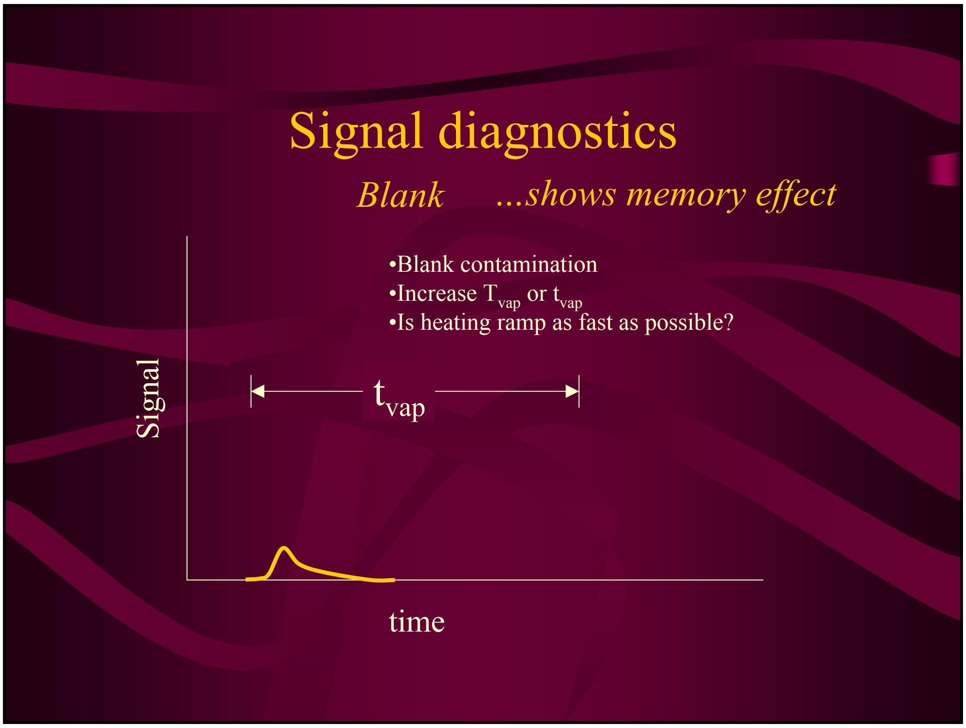




Signal diagnostics

Signal persists throughout ETV heating

Increase T_{vap} or t_{vap}



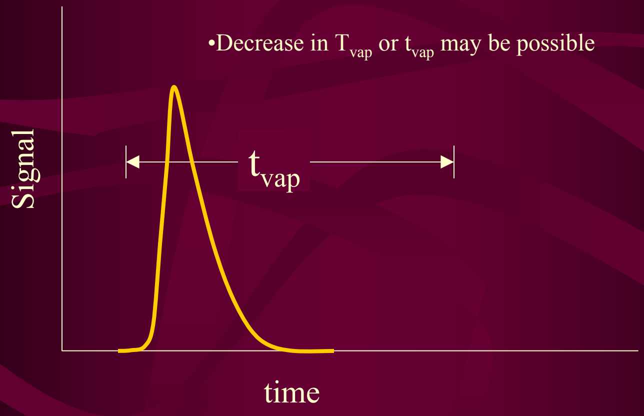
Signal diagnostics

Blank ...shows memory effect

- Blank contamination
- Increase T_{vap} or t_{vap}
- Is heating ramp as fast as possible?

Signal diagnostics

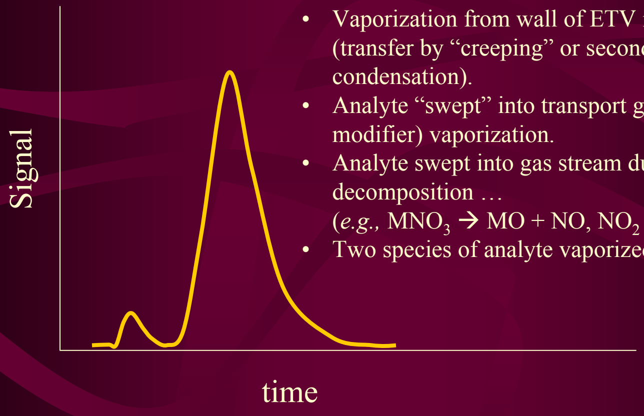
Signal width much shorter than vaporization time



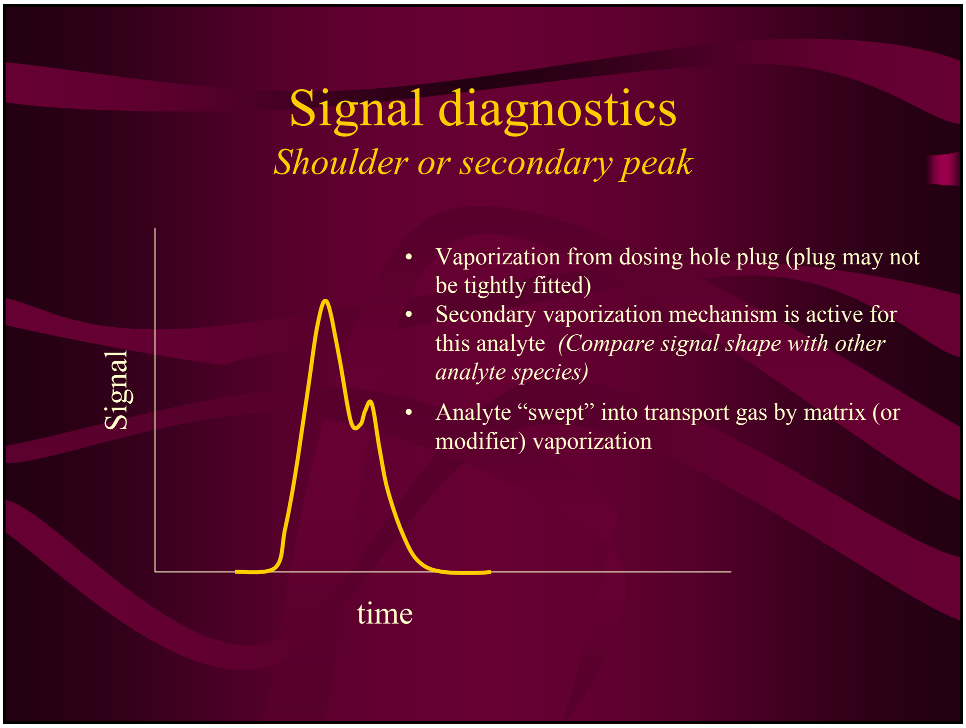
•Decrease in T_{vap} or t_{vap} may be possible

Signal diagnostics

Precursor peak



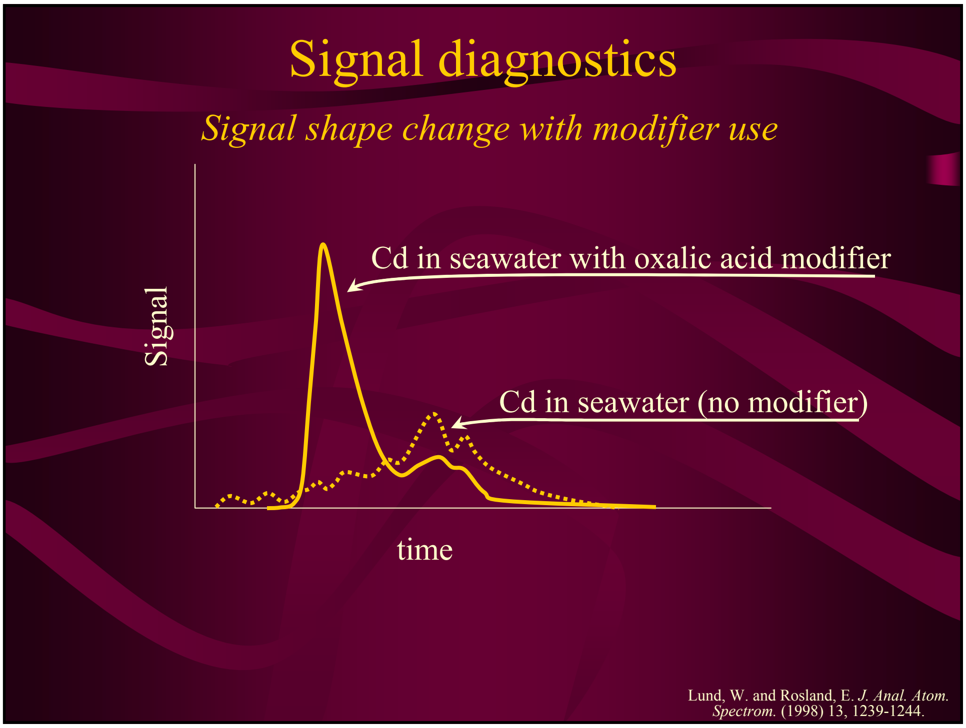
- Vaporization from wall of ETV if using a platform (transfer by "creeping" or secondary condensation).
- Analyte "swept" into transport gas by matrix (or modifier) vaporization.
- Analyte swept into gas stream during analyte decomposition …
  (*e.g.*, $MNO_3 \rightarrow MO + NO, NO_2, O_2$)
- Two species of analyte vaporized



Signal diagnostics

Shoulder or secondary peak

- Vaporization from dosing hole plug (plug may not be tightly fitted)
- Secondary vaporization mechanism is active for this analyte *(Compare signal shape with other analyte species)*
- Analyte "swept" into transport gas by matrix (or modifier) vaporization



Signal diagnostics

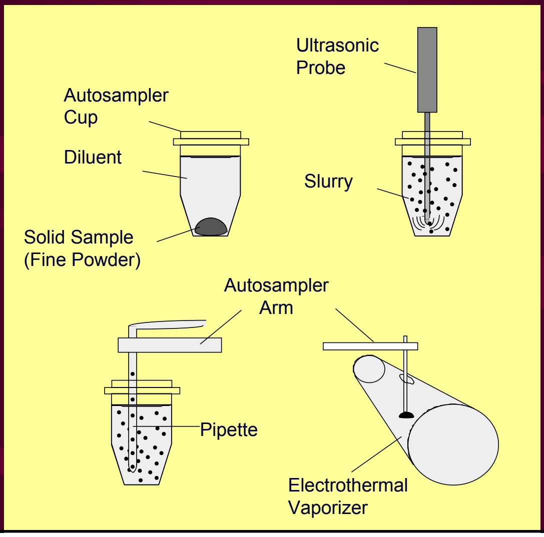
Signal shape change with modifier use

Cd in seawater with oxalic acid modifier

Cd in seawater (no modifier)

Lund, W. and Rosland, E. *J. Anal. Atom. Spectrom.* (1998) 13, 1239-1244.

Slurry sampling



Why Slurry Sampling ?

- Combines the benefits of solid sampling and liquid sampling
- No special tools are required
- Automation is straightforward
- Dilution is not a problem
- Slurries may be prepared in advance
- Slurry sampling saves time
- No one wants to do time consuming sample preparation (even with microwaves)

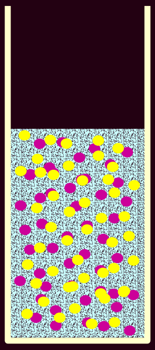
Approaches to Slurry Analyses

- Slurry Stabilization
  - Addition of a Thixotropic Agent
- Stir Bar Mixing
- Agitation (manual, wrist action shaker)
- Ultrasonic Mixing
  - Ultrasonic Bath
  - Hand Held Ultrasonic Probe
  - Automated Ultrasonic Probe System

Important Principles Related to Slurry Sampling

- **Density** - affects # particles injected, determines how long particles remain in suspension, the sampling depth, and determines the V_s/V_l ratio.
- **Particle Size** - affects pipetting, # particles injected, and the sampling depth (settling velocity)
- **Grinding** - improves homogeneity, increases the # of particles, aids extraction and avoids sedimentation errors
- **Analyte Partitioning** - provides insights into precision and helps determine the mass of solid represented by the analysis - used to calculate M_a
- **Slurry Mixing** - mechanical agitation provides most vigorous mixing. Mixing intensity must take into consideration particle size and density (may affect extraction)
- **Sampling Depth** - most critical if working with a high density material and there is a significant delay in the sample uptake
- **Homogeneity** - under optimum conditions sub-mg homogeneity assessments can be made

Sampling depth and particle settling



- Heavy
- Light

Sampling near the bottom better insures accurate sample of slurry

---

e.g., Homogeneity and Particle Size

- Particle size affects pipetting, the sampling depth, and the number of paritlces injected for analysis (small size is not a prerequisite -- 300-500 µm may be tolerated)
- Grinding techniques may prove useful (mortar grinding, teflon beads in polyethylene bottles, ball or jar mills, cryogenic grinding)
- Contamination risk should be minimized (avoid stainless steel)
- Samples most often should not be sieved

*** When analyzing unknown samples, a variety of weights should be used - Typical experimental design: 3 readings of 3 slurries; (10 mg/1mL; 20 mg/1 mL; 50 mg/1 mL)*

Optimize Slurry Preparations

- Grinding to decrease the particle size will:
  - improve slurry homogeneity
  - increase the number of particles
  - aid analyte extraction
  - and may help avoid sedimentation errors
- Knowledge of sample density provides info on:
  - the number of particles analyzed
  - how long particles will remain in suspension
  - the volume/volume ratio (affects pipetting accuracy)
- Knowledge about analyte extraction provides info about:
  - expected precision
  - the mass of solid represented by an analysis

Effect of Oxygen Ashing and Pd on Mn Signals - Oyster Tissue SRM

[C

O_2 ashing tips:

Ashing is a combustion reaction… not all materials combust!

Ash T $\leq$ 900°C (very dull red)

Use air or O_2 in sheath gas (Ar or N_2)

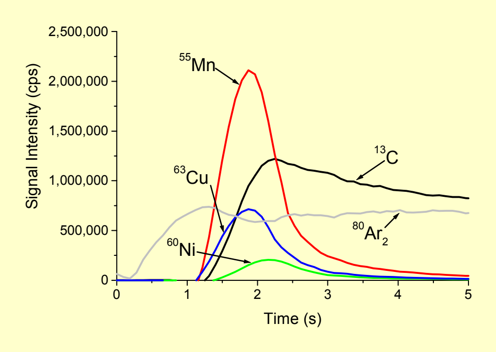
For ICP, O_2 sent to plasma may extinguish it (Keep dosing hole open or reduce O_2 concentration is problem)

Cool furnace down in O_2-containing gas

Flush of few sec all that is needed before atomization cycle.

USS-ETV-ICP-MS Signal Pulses

[SRM 1548 Total Diet; 1 µg Pd, 40 s Oxygen Ashing]



NIST SRM 1548 Total Diet

Concentration (µg /g)

	Mn	Ni	Cu
Total Diet	5.7 ± 0.3	0.44 ± 0.03	2.9 ± 0.2
Certified Range	5.2 ± 0.04	(0.41)	2.6 ± 0.3

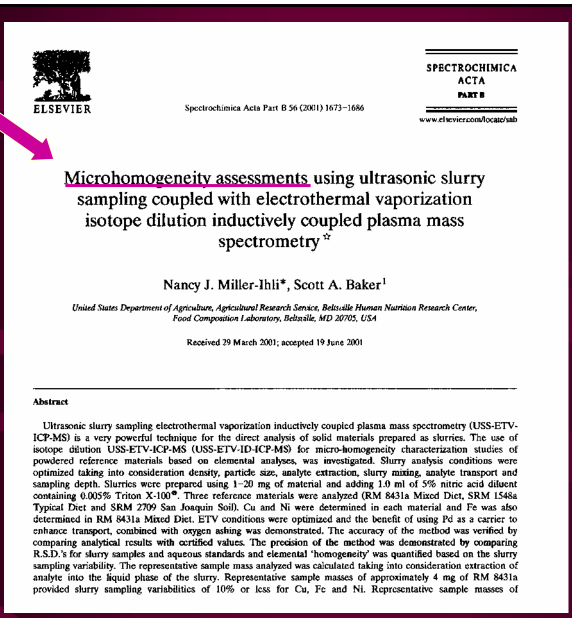
ETV-ICP-MS Quantitative Results

1 µg Pd, Oxygen Ashing, External Calibration

Concentration (µg/g)

Sample	V	Mn	Ni	Cu	Pb
SRM 1632a Coal Reference Value 1 mg / 1 mL	44 ± 3 44 ± 3	28.6 ± 4.0 28 ± 2	19.8 ± 2.2 19.4 ± 1.0	16.6 ± 4.0 16.5 ± 1.0	12.5 ± 0.2 12.4 ± 0.6
SRM 1548 Diet Reference Value 20 mg / 1 mL	0.52 ± 0.04 [0.68 ± 0.08]	5.2 ± 0.4 5.2 ± 0.4	0.48 ± 0.04 (0.41)	3.1 ± 0.1 2.6 ± 0.3	0.062 ± 0.004 (0.05)
SRM 1566a Oys Tis Reference Value 4 mg / 1 mL	5.8 ± 0.2 4.68 ± 0.15	14.2 ± 0.4 12.3 ± 1.5	1.9 ± 0.4 2.25 ± 0.44	76.4 ± 1.2 66.3 ± 4.3	0.47 ± 0.03 0.371 ± 0.014
LUTS-1 Reference Value 10.3 mg / 1 mL	0.257 ± 0.005 [0.17 ± 0.01]	1.30 ± 0.03 1.20 ± 0.13	0.213 ± 0.008 0.200 ± 0.034	Saturated 15.9 ± 1.2	0.022 ± 0.002 0.010 ± 0.002

* Values with uncertainties represent certified values, values in parentheses correspond to NIST information values, and values in square brackets correspond to concentrations determined by ICP-AES after acid digestion.



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Microhomogeneity assessments using ultrasonic slurry sampling coupled with electrothermal vaporization isotope dilution inductively coupled plasma mass spectrometry ☆

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Received 29 March 2001; accepted 19 June 2001

Abstract

Ultrasonic slurry sampling electrothermal vaporization inductively coupled plasma mass spectrometry (USS-ETV-ICP-MS) is a very powerful technique for the direct analysis of solid materials prepared as slurries. The use of isotope dilution USS-ETV-ICP-MS (USS-ETV-ID-ICP-MS) for micro-homogeneity characterization studies of powdered reference materials based on elemental analyses, was investigated. Slurry analysis conditions were optimized taking into consideration density, particle size, analyte extraction, slurry mixing, analyte transport and sampling depth. Slurries were prepared using 1–20 mg of material and adding 1.0 ml of 5% nitric acid diluent containing 0.005% Triton X-100®. Three reference materials were analyzed (RM 8431a Mixed Diet, SRM 1548a Typical Diet and SRM 2709 San Joaquin Soil). Cu and Ni were determined in each material and Fe was also determined in RM 8431a Mixed Diet. ETV conditions were optimized and the benefit of using Pd as a carrier to enhance transport, combined with oxygen ashing was demonstrated. The accuracy of the method was verified by comparing analytical results with certified values. The precision of the method was demonstrated by comparing R.S.D.'s for slurry samples and aqueous standards and elemental 'homogeneity' was quantified based on the slurry sampling variability. The representative sample mass analyzed was calculated taking into consideration extraction of analyte into the liquid phase of the slurry. Representative sample masses of approximately 4 mg of RM 8431a provided slurry sampling variabilities of 10% or less for Cu, Fe and Ni. Representative sample masses of

N. Miller-Ihli, S. Baker, *Spectrochim. Acta*, **56B**, 1673-1686.

General Conclusions

- ETV-ICP-MS may be used for quantitation and micro-homogeneity assessments (M_a of 0.2-0.5 mg; typically 3-6% RSD)
- Analysis conditions must be optimized (matrix modifier/carrier; selection of mass)
- Isotope Dilution proved to be the most useful calibration strategy for ETV-ICP-MS
- Pd/O_2 ashing prove useful for a wide range of matrices
- Slurry preparations must be optimized (sampling depth, mix time, sample mass, diluent, volume, material density, etc.)

Vapor Generation Techniques

Not just for ICP… *but* these approaches can be useful for ICP-based techniques

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Why Vapor Generation ?

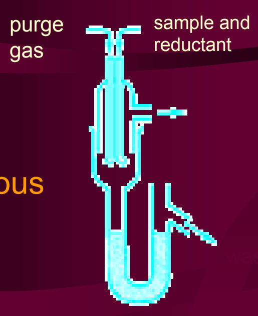
- enhanced transport efficiency: 2 → 100%
- amenable to automation
- compatible with preconcentration systems
- minimization/elimination of matrix interferences
- enhanced accuracy, sensitivity and precision
- enhanced selectivity - for speciation

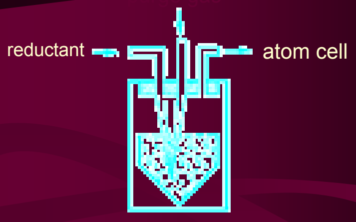
Vapor Generation Techniques

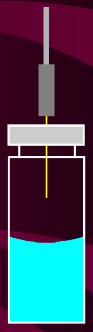
- batch systems: { bulk
  headspace (SPME)
- continuous generation
- segmented or FI systems
- solid sampling of endogenous species (SPME)

---

continuous

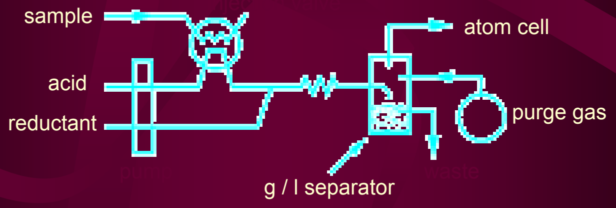


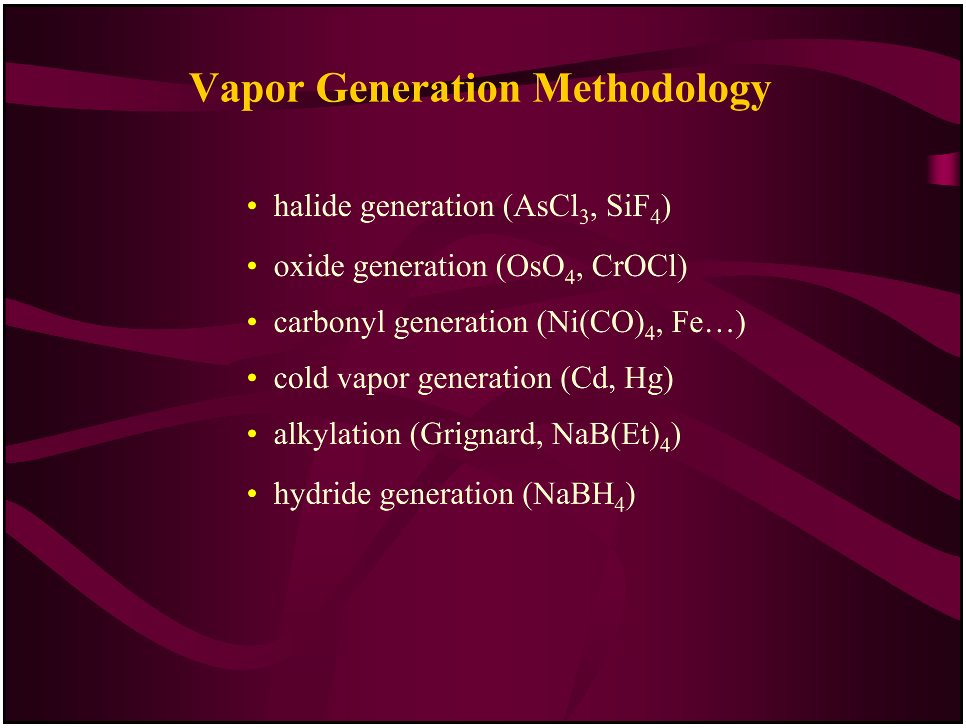




batch

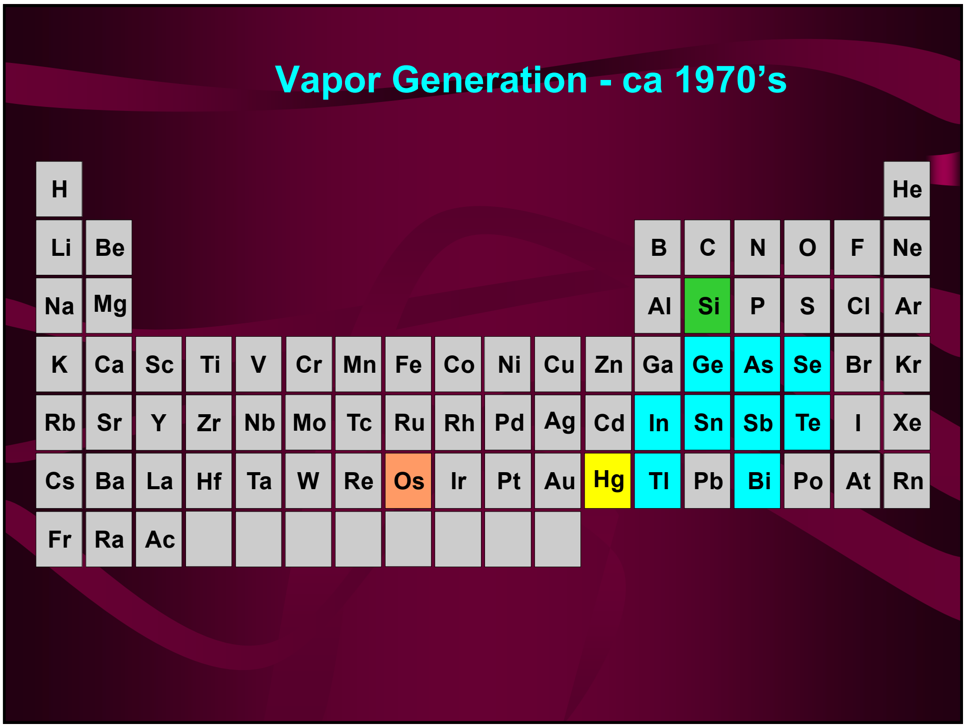
flow injection





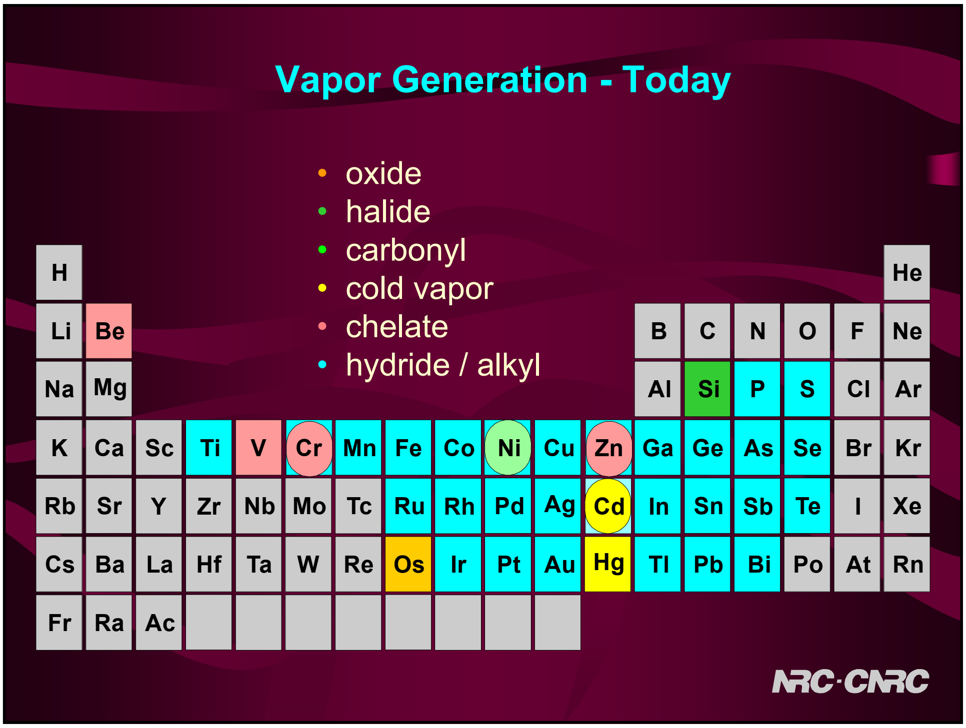
Vapor Generation Methodology

- halide generation ($AsCl_3$, SiF_4)
- oxide generation (OsO_4, CrOCl)
- carbonyl generation ($Ni(CO)_4$, Fe…)
- cold vapor generation (Cd, Hg)
- alkylation (Grignard, $NaB(Et)_4$)
- hydride generation ($NaBH_4$)



Vapor Generation - ca 1970’s

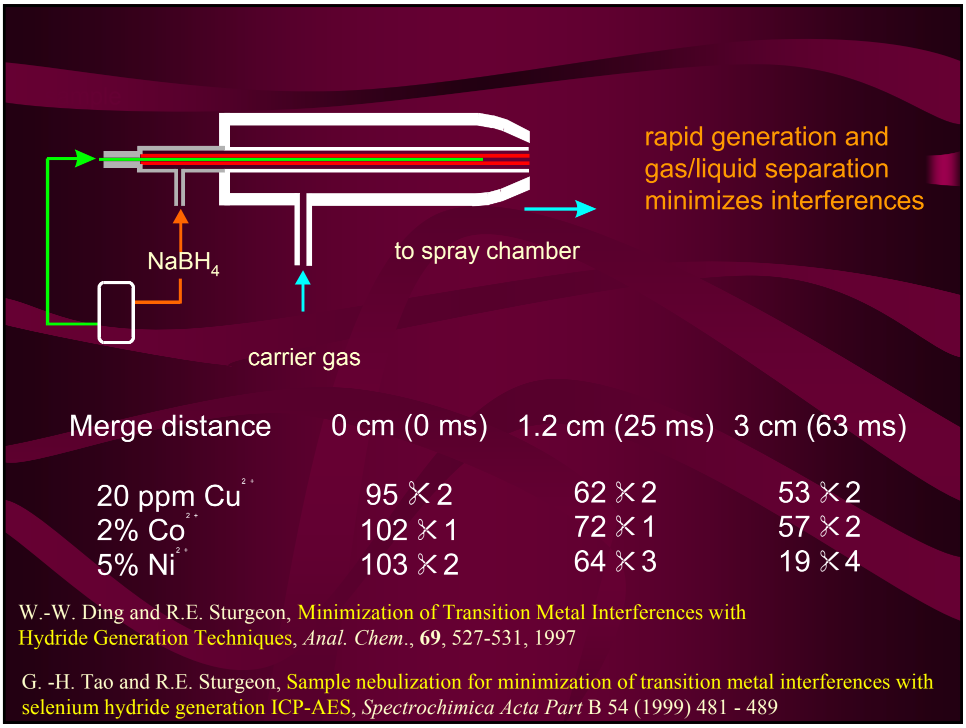
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															



Vapor Generation - Today

- oxide
- halide
- carbonyl
- cold vapor
- chelate
- hydride / alkyl

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

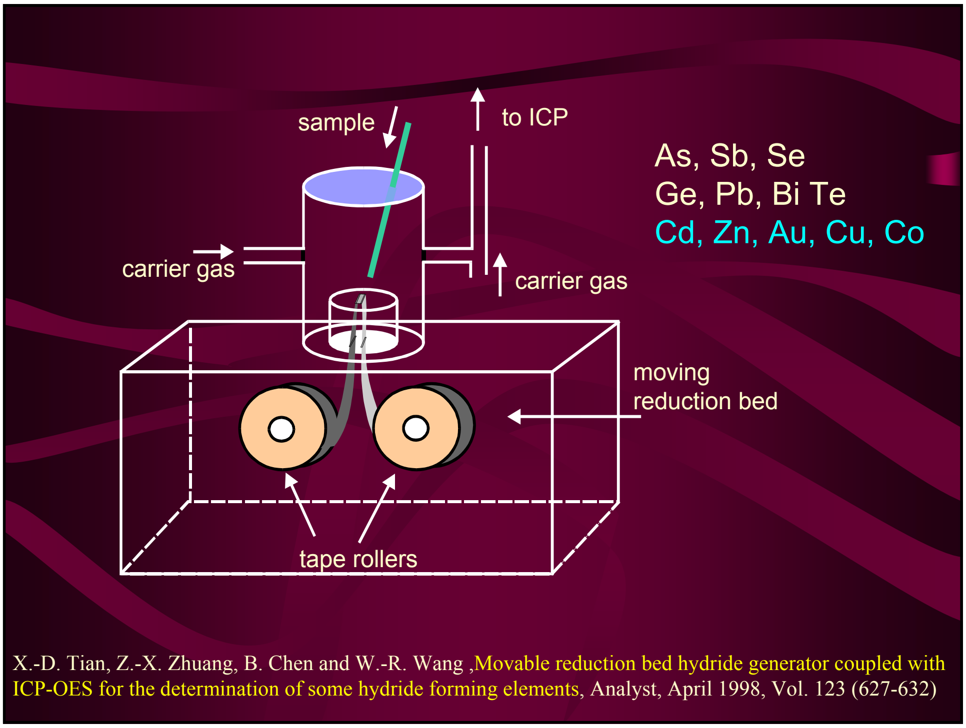


rapid generation and gas/liquid separation minimizes interferences

Merge distance	0 cm (0 ms)	1.2 cm (25 ms)	3 cm (63 ms)
20 ppm Cu^{2+}	95 ⨉ 2	62 ⨉ 2	53 ⨉ 2
2% Co^{2+}	102 ⨉ 1	72 ⨉ 1	57 ⨉ 2
5% Ni^{2+}	103 ⨉ 2	64 ⨉ 3	19 ⨉ 4

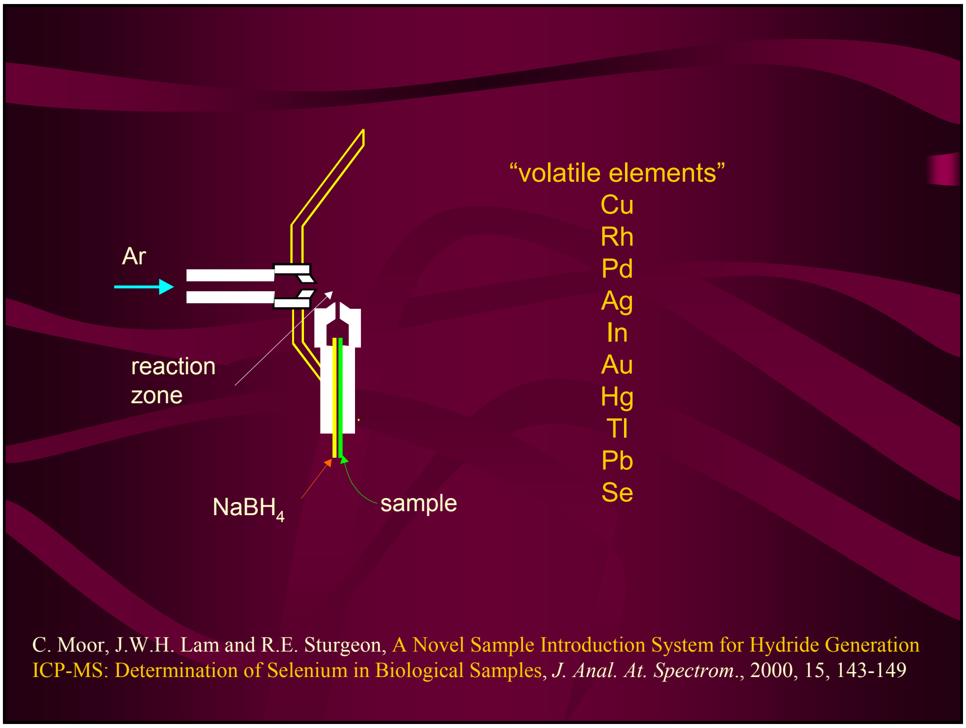
W.-W. Ding and R.E. Sturgeon, Minimization of Transition Metal Interferences with Hydride Generation Techniques, *Anal. Chem.*, **69**, 527-531, 1997

G. -H. Tao and R.E. Sturgeon, Sample nebulization for minimization of transition metal interferences with selenium hydride generation ICP-AES, *Spectrochimica Acta Part* B 54 (1999) 481 - 489



As, Sb, Se
Ge, Pb, Bi Te
Cd, Zn, Au, Cu, Co

X.-D. Tian, Z.-X. Zhuang, B. Chen and W.-R. Wang ,Movable reduction bed hydride generator coupled with ICP-OES for the determination of some hydride forming elements, Analyst, April 1998, Vol. 123 (627-632)



"volatile elements"
Cu
Rh
Pd
Ag
In
Au
Hg
Tl
Pb
Se

C. Moor, J.W.H. Lam and R.E. Sturgeon, A Novel Sample Introduction System for Hydride Generation ICP-MS: Determination of Selenium in Biological Samples, *J. Anal. At. Spectrom.*, 2000, 15, 143-149

Xiaoguang Du and Shukun Xu, Flow-injection chemical vapor-generating procedure for the determination of Au by atomic absorption spectrometry, *Fresenius J Anal Chem* (2001) **370**: 1065 - 1070

Automated FIA system using DDTC to enhance response in a 1000°C quartz cell for analysis of ore sample digests by standard additions

LOD: 24 ppb 2.0% RSD @ 2 ppm

Pawel Pohl and Wieslaw Zyrnicki, Study of chemical vapor generation of Au, Pd and Pt by inductively coupled plasma optical emission spectrometry, *J. Anal. At. Spectrom.* (2001) **16**, 1442-1445

Pawel Pohl and Wieslaw Zyrnicki, On the transport of some metals into inductively coupled plasma during hydride generation process, *Analyt. Chim. Acta* **429** (2001) 135-143

Report enhanced signals for Cr, Fe and Ni

X. Duan, R.L. McLaughlin, I.D. Brindle and A. Conn, Investigations into the generation of Ag, Au, Cd, Co, Cu, Ni, Sn and Zn by vapor generation and their determination by ICP-AES, together with a mass spectrometric study of volatile species. Determination of Ag, Au, Co, Cu, Ni and Zn in iron, *J. Anal. At. Spectrom.*, 2002, **17**, 227-231

Generated analytes are short-lived species that decompose into atoms. If they are not rapidly removed from solution, then aggregation of the atoms will take place

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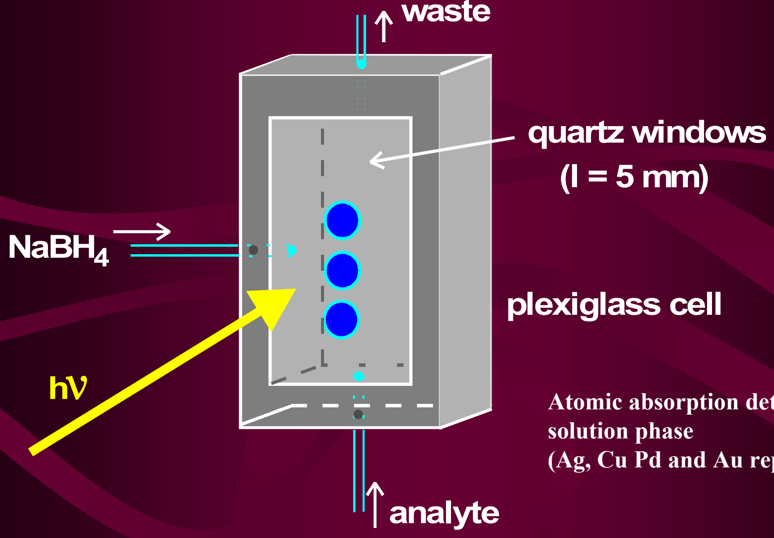
Solution Phase Reduction



waste

quartz windows

(l = 5 mm)

$NaBH_4$

plexiglass cell

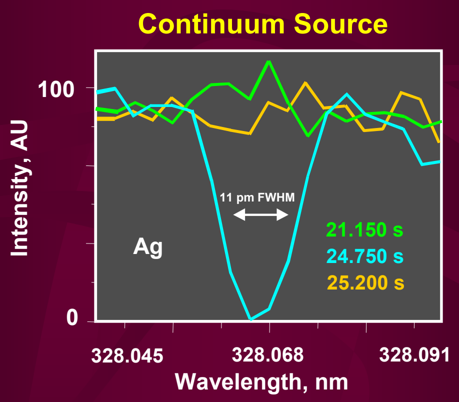
hν

analyte

Atomic absorption detected in solution phase
(Ag, Cu Pd and Au reported)

Nikolai Panichev and Ralph E. Sturgeon, Atomic Absorption by Free Atoms in Solution Following Chemical Reduction from the Ionic State, *Anal. Chem.* 1998, **70**, 1670-1676

Are atoms in solution?


Continuum Source

Nikolai Panichev and Ralph E. Sturgeon, Atomic Absorption by Free Atoms in Solution Following Chemical Reduction from the Ionic State, *Anal. Chem*. 1998, **70**, 1670-1676

Aquo- Ion Reduction

$$NaBH_4 + 3\,H_2O + HCl \longrightarrow H_3BO_3 + NaCl + 8\,H\cdot \xrightarrow{E^{m+}} EH_n + H_2$$

$$M^+ + e^-_{aq} \longrightarrow M^o$$

$$n\,M^o + M^+ \longrightarrow M^+_{n+1}$$

$$m\,M \longrightarrow M_m$$

$$M^o + n\,H. \longrightarrow MH_n$$

Conclusions

- Expanded elemental coverage
- Vapor generation provides thriving research opportunities
- Development of new generation techniques
- New sampling approaches for SPME
- New approaches for preconcentration

Acknowledgements

- **Dr. Ralph Stugeon** (National Research Council; Ottawa, Canada)
- **Dr. Nancy Miller-Ihli** (USDA Nutrient Composition Laboratory)
- **Dr. Conrad Gregoire** (Geological Survey of Canada)

- **Dr. Gulay Ertas**
- **Mr. William Balsanek**
- Former students**: Drs. D. Langer, J. Venable**

- **Yngvar Thomassen** and ***the Nordic Conference on Plasma Spectrochemistry***

- **National Science Foundation**