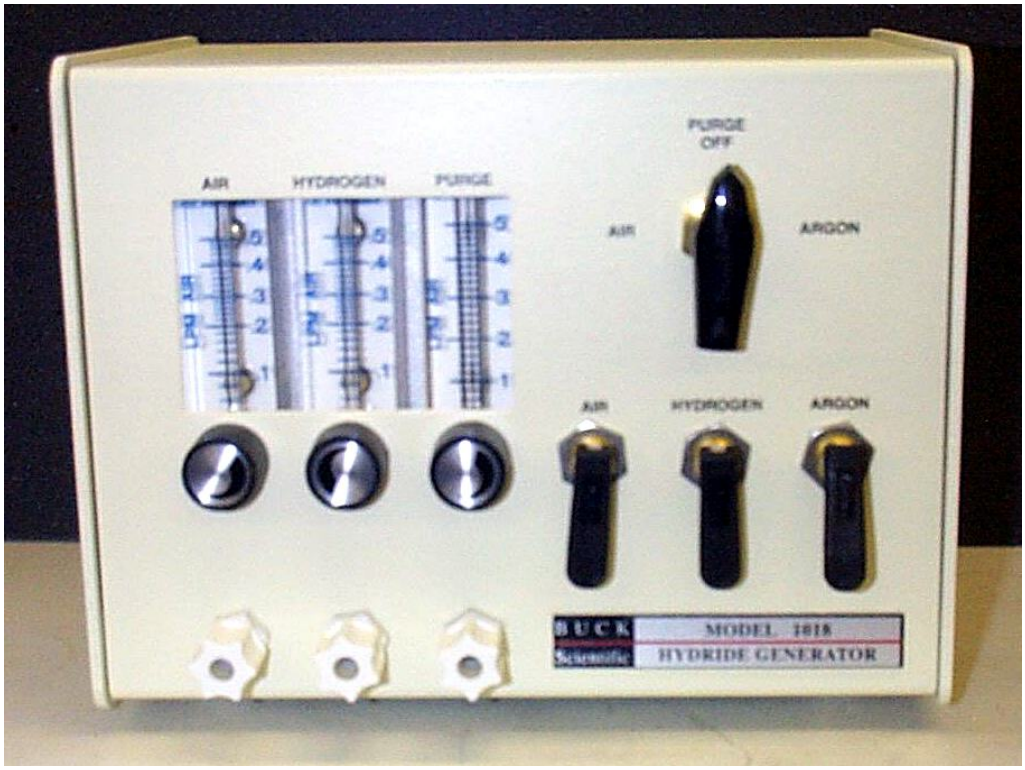
BUCK SCIENTIFIC

Model 1018

Combination Hydride/Cold Vapor Generator
for low-level determination of Arsenic, Selenium and Mercury

INSTALLATION AND OPERATION MANUAL

5/2008
Rev.6



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NOTES:

1. When using Swagelok tube fittings it is not necessary to use pipe tape or to tighten the fittings tighter than 1 to 1 1/4 turn beyond finger tight initially to make a gas-tight seal.
   -=> NOTE: Do NOT over-tighten or the brass fittings will strip or damage the tubing!!
2. Check all gas connections for leaks using a dilute soapy water solution.
3. It will be easier to connect the silicone tubing to the glassware if you first wet the fittings on the glassware before attaching the tubing to them.
4. These following instructions assume that the user is familiar with the operation of the AA instrument.
5. Once the hydride system has been plumbed (gas connected) to the AA & Quartz T-Tube / Absorption Tube, it can be left connected permanently so that you can switch between normal AA flame operation and hydride/cold vapor operation at any time.
6. You can use the standard Air/Acetylene Flame to create the Atomic Vapor in the T-Tube for the Hydride reactions, to avoid running an Argon/Hydrogen flame instead of Air/Acetylene.

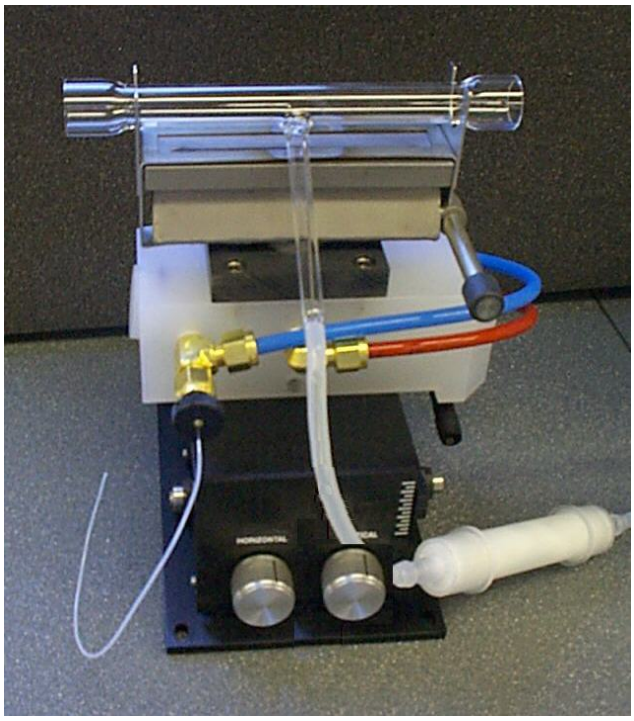
INSTALLATION:

1. Position the ***Hydride unit*** in such a way that you can keep the length of the tubing to the ***Quartz flow cell*** **(for CV-Hg)** ***or tee tube*** **(for Hydride)** as short as possible but not so close as to interfere with the operation of the instrument. An appropriate length is 12”-20” (see step-5).
2. Use the ¼” Nylon tubing and brass Swagelok fittings supplied with the system (see picture for details) to make the gas connections with the appropriate gases (Argon / Nitrogen, Air, Hydrogen) on the **back** of the unit.

3. Install the desired ***H-C Lamp*** into the instrument and allow 15-20 minutes for the lamp to warm up. Optimize the instrument according to the instruction manual for your instrument. For 210/211-VGP customers, recall element files [As-Hydride_193.7] or [Se-Hydride_196.0], set conditions as noted for best results and automatic peak integration:

ELEMENT	WAVELENGTH (nm)	SLIT (A)	HCL CURRENT (mA)
Arsenic	193.7	7	Per file setup, or 5.0
Selenium	196.0	7	Per file setup, or 6.0
Antimony	217.6	2	Per file setup, or 5.0
Mercury	253.7	7	Per file setup, or 3.0

4. Install the sheet metal ***tee tube holder*** on the burner head. Next cut a 3" length of the ¼" O.D. Silicone tubing and slip it on to the ***Quartz flow cell or tee tube inlet***. Connect the other end of the tubing to the plastic ***moisture trap tube***. Insert the ***flow cell or tee tube*** into its holder and align so that the lamp image is centered through the tube for maximum energy.



QUARTZ T-Tube for HYDRIDE Generation method

Absorption Cell for Cold Vapor Mercury method

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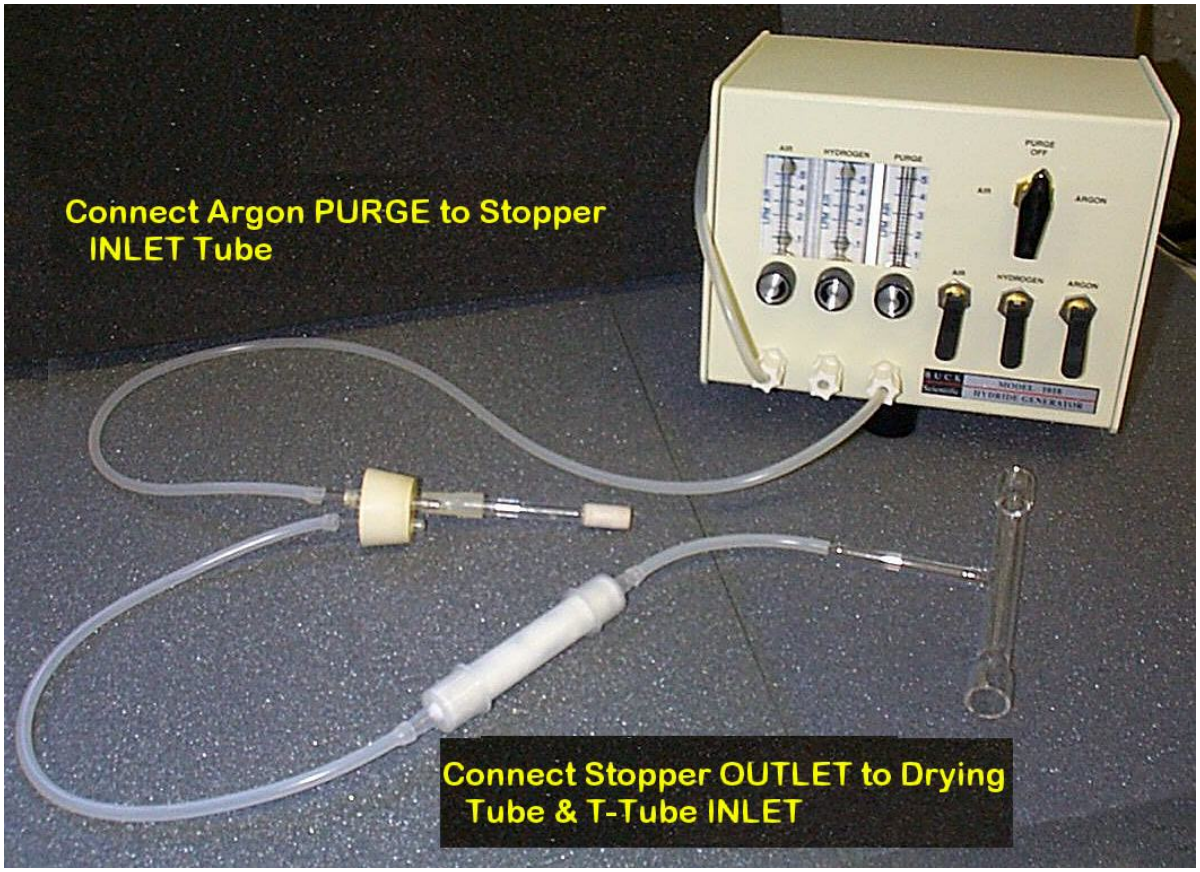
5. Use a convenient length of ¼" silicone tubing to connect the ***moisture trap tube*** to the reaction outlet line of the reaction flask. The ***moisture trap*** should be filled with one or two lint-free tissues to trap any liquid aerosol coming from the reaction flask. Do NOT use any chemical dryers!

6. Once the connections are complete turn the flame on to a lean blue condition for HYDRIDE or just proceed to the reaction for COLD VAPOR (no Flame needed).

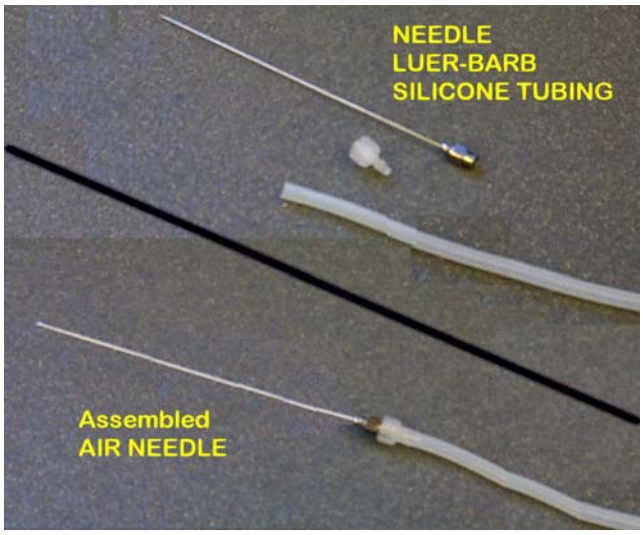
STOPPER ASSEMBLY / Gas Line Connections:

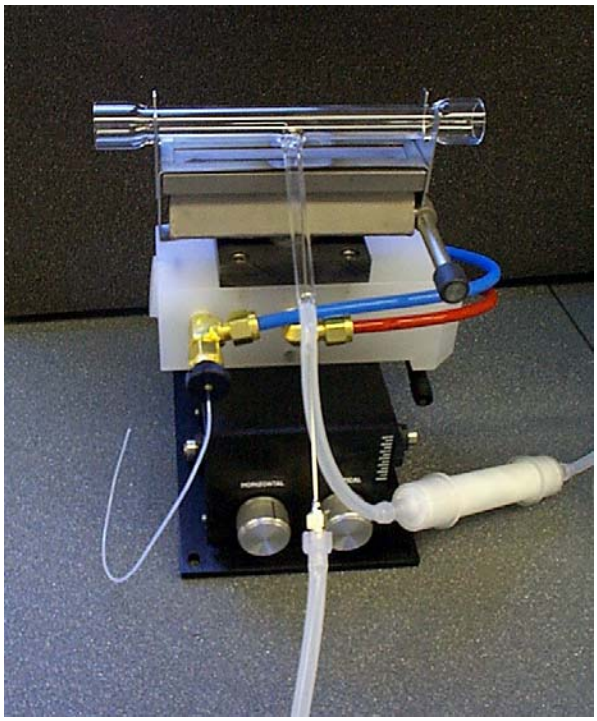
1. Using the ¼" Silicone tubing, connect the ARGON Purge Gas OUTLET from the FRONT of the 1018 unit to the Bubbler INLET tube on Stopper Assembly for the reaction flask.
2. Use a short, but convenient length of silicone tubing (12"-20") from the Gas OUTLET tube of the Stopper Assembly to the end of the ***moisture trap tube***.

3. The outlet side of the ***moisture trap*** tube should be connected to the inlet of the on to the ***Quartz flow cell or tee tube.***



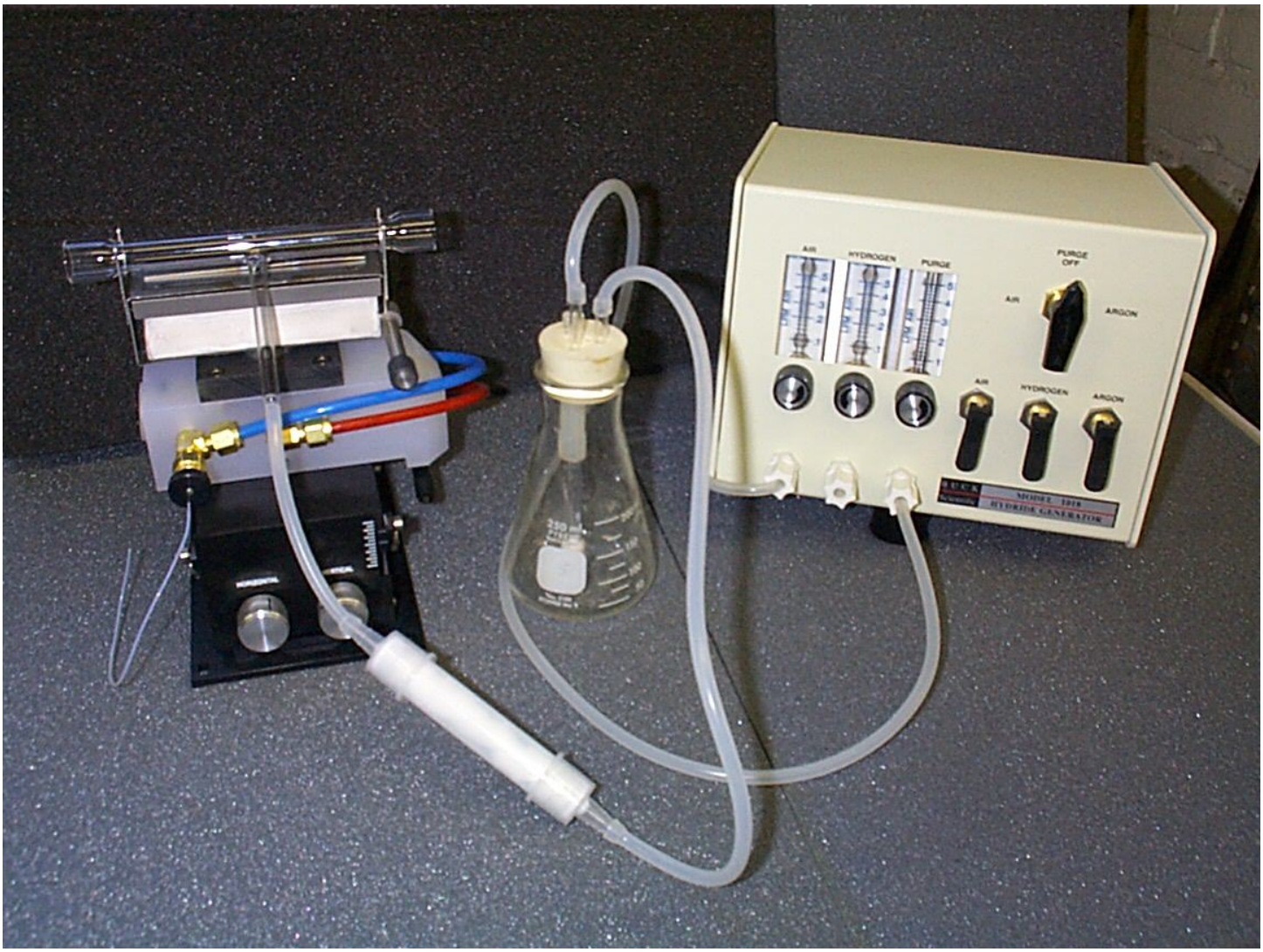
4. ***OPTION:*** To MAXIMIZE the response for the Arsenic & Selenium by the Hydride Generation reaction, a SUPPLEMENTAL Gas FLOW of AIR is often used to INCREASE the Combustion Rate of the Hydride in the Quartz T-Tube. To use this feature =
   A) Connect the the ¼" Silicone tubing to the Air Gas OUTLET from the front of the 1018 unit.
   B) Keep the length of this line to ~20", and insert the other end into the Barbed-LuerLock Fitting for the "Air Injection Needle" (see Picture-3 for details).
   C) CAREFULLY insert the pointed end of the Needle into the Silicone Tubing near the INLET of the Quartz T-Tube.
   D) Make adjustments to the Argon and Air Flows as described below to optimize the SIGNAL for the Element of interest.
5. **You are now ready to begin the analysis of the Sample.**





COMPLETED Hydride Generation Assembly

[Optional AIR Injection for increased Sensitivity discussed below]



-=> NOTE: ***The Model-1018 Hydride Generator system includes an OPTION to use HYDROGEN Gas to supplement the Flame for complete decomposition of the Hydride species. This was developed to meet the requirements of a proposed USEPA Method that has not been published yet, so BUCK does not recommend it's use at this time.***

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***Running the HYDRIDE Analysis* (Arsenic or Selenium):**

1. Prepare FRESH reagents as noted below. ALWAYS keep track of the AGE of your solutions!!
   REDUCING AGENT = Weigh 0.5 grams of Sodium Hydroxide into a 4oz. HDPE bottle. Add ~25ml. DI Water and swirl to dissolve. Add 5 grams of **fresh** Sodium Borohydride into the 100ml. bottle, swirl gently (do ***not*** cap & shake!) to dissolve. Add DI Water to ~100ml. volume, cap and keep cool. This 5% NaBH4 solution is stable for approx. 30 days.

   ACIDIFICATION SOLUTION = Add 100ml. of Concentrated H2SO4 to 200ml. of deionized (DI) water and allow to cool. Carefully add 150ml. of Concentrated HCl and swirl to mix. Dilute to 500ml. with (DI) water. This solution is usable for approximately 3 months, but may become contaminated under non-ideal conditions. If blank values become too high, discard and make fresh Acid Solution.

2. Make sure the Argon Purge and Air OUTLET lines from the front of the 1018 unit are connected to the Bubbler INLET and Air Needle, respectively.

3. Adjust the gas flows to the following settings as a starting point, and raise or lower as needed to optimize the analysis [see cover picture for details of the flowmeter front panel assembly]:

Arsenic:	Purge (Argon) = 3.0-4.0	Air = ~0.5 (for better Sensitivity)
Selenium:	Purge (Argon) = 3.0-4.0	Air = ~0.5 (for better Sensitivity)
Antimony:	Purge (Argon) = 2.5-3.5	Air = ~0.5 (for better Sensitivity)

   -=> *NOTE: These are SUGGESTED settings, but the optimum gas flows will depend on the volume of the sample, the concentration of the analyte and the composition of the sample matrix (background). Please adjust to provide the most accurate and reproducible peak shape.*

4. Pipet an aliquot (5-50 ml.) of a Standard solution into the reaction flask
   Suggested calibrations for a decent 2nd order curve-fit = 5PPB, 50PPB and 250PPB.

5. IF NEEDED; add ~0.25gms of a Secondary Reductant (Ascorbic Acid, Potassium Iodide or Hydroxylamine) to vessel and warm to 75-80^{o}C if possible; or use hot water for the dilution of the sample. **This step is only needed if the Sample results are not consistent.** Add 25ml. of the Mixed Acid to flask and dilute to ~100-150ml. Start flow of Argon to bubbler.

6. With the gases bubbling through the reaction flask, press the A/Z key to zero the energy on the 210/211-AA. Fill a syringe with 5ml. of the 5% Sodium Borohydride Reductant solution, insert into the septum tube of the stopper assembly, press the READ key and then slowly, but steadily, inject this reductant onto the surface of the solution in the flask, allowing the Reductant to react and agitate the mixture. For best results, Introduce the Reductant on TOP of the sample solution at ~1ml/sec to control the rate of reaction, and swirl the flask gently to insure complete mixing.

7. After the 10-20 seconds needed to record the signal, allow the reading to get back or close to zero after the

integration, turn off the Argon bubbler flow and remove the reaction flask. Rinse twice with 5% HCl, and wash down the bubbler tube with 5% HCl + 3% H2O2 in a wash bottle. Reassemble and continue with next solution.

8. Start with a Reagent Blank run to insure the quality of the materials used, followed by the appropriate Standards for calibration; then **take 8-12 integrated sample readings**, afterwards checking a Standard.

9. Use the Integrated Area of the Peak to establish a Calibration Curve, and interpolate Sample Peak Areas relative to this to get the appropriate concentrations using the 210/211 Calibration option.

10. Be sure to rinse off the Bubbler assembly and the Reaction Flask well with DI Water and 2-5% Nitric Acid when finished to remove all traces of Reagents that may affect future analyses .

Running the COLD VAPOR Analysis (Mercury):

1. Place a mercury H-C Lamp in holder and allow to warm up for ~15 minutes. For 210/211-VGP customers recall file [Hg-CV_253.7].

2. Prepare FRESH reagents as noted below. ALWAYS keep track of the AGE of your solutions!!

   REDUCING AGENT = Place 10 grams of FRESH Stannous Chloride (looks yellow, not chalky) into an empty, acid-cleaned 100 ml. plastic (HDPE) bottle, and 30 ml. concentrated HCl, ~1 gms Tin metal (foil, shot, mossy; NOT powder) and swirl/stir to dissolve the $SnCl_2$. When dissolved (some solutions will be milky due to some SnO_2 oxide present, this does not present a problem), add ~75 ml. good quality DI water. Swirl gently to mix. This 10% solution is stable and usable for ~30 days.

   ACIDIFICATION SOLUTION = Add 100ml. of Concentrated H2SO4 to 200ml. of deionized (DI) water and allow to cool. Carefully add 150ml. of Concentrated HCl and swirl to mix. Dilute to 500ml. with (DI) water. This solution is usable for approximately 3 months, but may become contaminated under non-ideal conditions. If blank values become too high, discard and make fresh Acid Solution.

3. Connect the Argon Purge OUTLET line from the front of the 1018 unit directly into the Bubbler line of the stopper assembly [see diagram #4 for enlarged details for stopper assembly].

4. Adjust the gas flows to the following settings as a starting point, and raise or lower as needed to optimize the analysis [see diagram #1 for details of the flowmeter front panel assembly]:
   Mercury: Purge (Argon) = 20-50 Air = [not used]

   -=> *NOTE: These are SUGGESTED settings, but the optimum gas flows will depend on the volume of the sample, the concentration of the analyte and the composition of the sample matrix (background). Please adjust to provide the most accurate and reproducible peak shape.*

5. Pipet an aliquot (5-50 ml.) of a Standard solution into the reaction flask.
   Suggested calibrations for a 2^{nd} order curve-fit = 1.0PPB, 10PPB and 25PPB.

6. With the Air or Argon gas bubbling through the reaction flask, press the A/Z key to zero the energy on the 210/211-AA. Fill a syringe with 5ml. of the 10% Stannous Chloride Reductant solution, insert into the septum tube of the stopper assembly, press the READ key and then slowly, but steadily, inject reductant onto the surface of the solution, allowing the Reductant to react with the mixture. For best results, Introduce the Reductant on TOP of the sample solution at ~1ml/sec to control the rate of reaction, and swirl the flask gently to insure complete mixing.

7. After the 10-20 seconds needed to record the signal, allow the reading to get back or close to zero after the integration, turn off the Argon bubbler flow and remove the reaction flask. Rinse twice with 5% HCl, and wash down the bubbler tube with 5% HCl + 3% H2O2 in a wash bottle. Reassemble and continue with next solution.

8. Start with a Reagent Blank run to insure the quality of the materials used, followed by the appropriate Standards for calibration; then **take 8-12 integrated sample readings**, afterwards checking a Standard.

9. Use the Integrated Area of the Peak to establish a Calibration Curve, and interpolate Sample Peak Areas relative to this to get the appropriate concentrations using the 210/211 Calibration option.

10. Be sure to rinse off the Bubbler assembly and the Reaction Flask well with DI Water and 2-5% Nitric Acid when finished to remove all traces of Reagents that may affect future analyses.

MODEL 1018 PACKING LIST:

*1	Hydride Unit box
*1	Tee tube holder 420-1034
*4	250ml reaction flask 400-0250
*1	Adapter and bubbler assembly 400-0100
*1	200mm flow cell 420-1014
*1	Quartz Tee tube 420-1016
*1	Moisture trap 400-0400
*2	10', 1/4" O.D. black nycoil nylon tubing
*1	10', 1/4" O.D. red nycoil nylon tubing
*1	10', 1/4" O.D. silicon tubing
*6	1/4" nuts with ferrules
*10	10cc syringes
*1	Needle Assembly
*1	Y Fitting

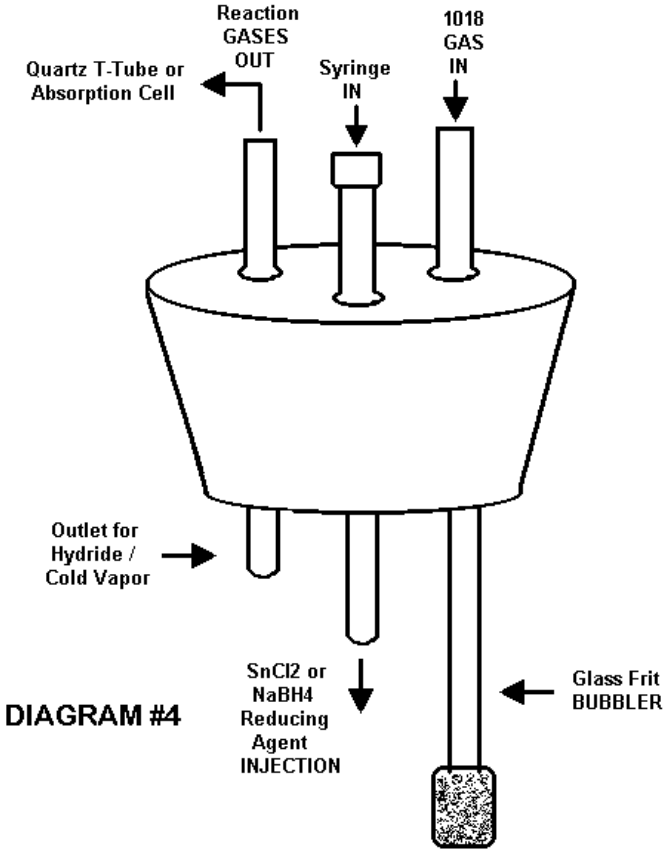

DIAGRAM #4

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Standardized BATCH Hydride Procedure for As, Se & Sb:

(for the Buck 1018 Combo Analyzer w/ 210-AA w/ V3.8+ Software)

** NOTE: Refer to proper 210 Quick-Guide for general instrumental settings.*

[1] Place Arsenic/Selenium/Antimony lamp in holder and allow to warm up for ~10-30 minutes. Load the appropriate Library File(s) from the 210-AA software [As-Hydride-193.7, Se-Hydride-196.0 or Sb-Hydride-207.0] into the correct Lamp position. Connect Hydride delivery line from the 1018 Assembly to the Quartz T-Tube & place over Burner Head in metal bracket. Adjust the H-C Lamp beam position for maximum energy.
-=> NOTE: Prepare all Reagent solutions FRESH! Replace when precipitates form & recoveries vary.

[2] Weigh 0.5 grams of Sodium Hydroxide into a 4oz/100ml. HDPE bottle. Add ~25ml. DI Water and swirl to dissolve. Add 5 grams of **fresh** Sodium Borohydride into the 100ml. bottle, swirl gently (do not cap & shake!) to dissolve. Add DI Water to ~100ml., cap and keep cool. This solution is stable for approx. 30 days.

[3] Mix 200ml. H2O, 100ml. H2SO4; let cool then carefully add 150ml. HCl; swirl to mix and dilute to ~500ml. final volume. After measuring the Sample into the Reaction Flask, add 25ml. of this acid mixture and bring the total volume to ~100ml. with DI Water. This Mixed Acid solution is usable for approx. 3 months, but will pick up contamination rapidly in most cases; so discard and make fresh as your Blank value increases.

[4] Pipet an aliquot (5-50 ml.) of a Standard solution into the reaction flask.

[5] IF NEEDED; add ~0.25gms of a Secondary Reductant (Ascorbic Acid, Potassium Iodide or Hydroxylamine) to vessel and warm to 75-80 ^{o}C if possible; or use hot water for the dilution of the sample. **This step is only needed if the Sample results are not consistent.** Add 25ml. of the Mixed Acid to flask and dilute to ~100-150ml. Start flow of Argon to bubbler.

[6] Zero the energy on the 210-AA, then slowly, but steadily, inject 5 ml. of the 5% Sodium Borohydride Reductant solution onto the surface of the solution in the flask with a syringe, allowing the Reductant to react and agitate the mixture. Introduce the Reductant on TOP of the sample solution at ~1ml/sec to control the rate of reaction, and start taking signal integrations at this time by pressing the READ key to get time window.

[7] Allow the reading to get back or close to zero after the integration, turn off the Argon bubbler flow and remove the reaction flask. Rinse twice with 5% HCl, and wash down the bubbler tube with 5% HCl + 3% H2O2 in a wash bottle. Reassemble and continue with next solution.

[8] Start with a Reagent Blank run to insure the quality of the materials used, followed by the appropriate Standards for calibration; then take 8-12 integrated sample readings, afterwards checking a Standard.

[9] Use the Integrated Area of the Peak to establish a Calibration Curve, and interpolate Sample Peak Areas relative to this to get the appropriate concentrations.

[10] Be sure to rinse off the Bubbler assembly and the Reaction Flask well with DI Water and 2-5% Nitric Acid when finished to remove all traces of Reagents that may affect future analyses.

CHEMISTRY CONSIDERATIONS:

Most NATURALLY occurring Arsenic & Selenium are present in the LOWER Valence State, to As^{+3} / Se^{+4}, but a vigorous "Oxidative" digestion of such samples can oxidize them to their HIGHER states; As^{+5} / Se^{+6}. Under these circumstances, the $NaBH_4$ gives only a PARTIAL reduction to the Hydride, and you will get either LOW results or see a "double Peak" during the measurement as the level fluctuates between the lower Valence and higher Valence reactions. Using either Potassium Iodide (KI) or Ascorbic Acid will "pre-reduce" the HIGHER Valences to their more stable LOWER states.

Standardized BATCH Cold-Vapor Procedure for Hg:

(for the Buck 1018 Combo Analyzer w/ 210-AA w/ V3.8+ Software)

** NOTE: Refer to proper 210 Quick-Guide for general instrumental settings.*

[1] Place BUCK Mercury H-C Lamp in a Lamp socket, load the "Hg-CV-253.7" element file from Library & allow to warm up ~15-30 minutes for best stability. Either place the 200mm. Adsorption Tube on the metal bracket over the Burner Head, or use the alternative mount (depending on the AA instrument you are using). Optimize the Wavelength (253.6 nm) & H-C Lamp position through the Tube for maximum energy. Make sure all components of the Cold Vapor system are warmed up to room temperature (>20oC) or possible condensation and long flush times may occur. Make sure Drying Tube is filled with Kim-Wipes or other clean paper to block any aerosol (mist) that may come through the Bubbler assembly line.

[2] Mix 200ml. H2O, 100ml. H2SO4; let cool then carefully add 150ml. HCl; swirl to mix and dilute to ~500ml. final volume. After measuring the Sample into the Reaction Flask, add 25ml. of this acid mixture and bring the total volume to ~100ml. with DI Water. This Mixed Acid solution is usable for approx. 3 months, but will pick up contamination rapidly in most cases; so discard and make fresh as your Blank value increases.

[3] Place 10 grams of FRESH Stannous Chloride (looks yellow, not chalky white) into an empty, acid-cleaned 100 ml. plastic (HDPE) bottle, and 30 ml. concentrated HCl, ~1 gms Tin metal (foil, shot, mossy; NOT powder) and swirl/stir to dissolve the SnCl2. When dissolved (some solutions will be milky due to some SnO2 oxide present, this does not present a problem), add ~75 ml. good quality DI water. Swirl gently to mix. This solution is stable and usable for ~10-20 days.

[4] Prepare a series of Standards at 5, 10, 25, 50, 100 PPB (ug/L).
Prepare Samples as recommended to produce ionic Mercury.
Warm a large Beaker of DI water on a hotplate to ~50^{o}C for potential use to dilute Sample solutions.

[5] Pipet an aliquot (10-50 ml.) of the prepared Reagent Blank or Standard solution into the reaction flask. Add 20ml. of the Mixed Acid solution to the flask, and bring the total volume up to ~100-150ml. with a DI water. Insert the Bubbler Assembly into the top of the Reaction Flask.

[6] Start Argon bubbler, and prepare to set up the Calibration Curve by pressing the <A/Z> key to Auto-Zero the energy, press the <READ> or <ENTER> key to start the data integration (depending on which screen you are in) then steadily, inject 5 ml. of the 10% Stannous Chloride Reductant solution into the septum of the flask stopper assembly with a syringe over 5 seconds.

[7] Allow the reading to get back or close to zero, turn off Argon bubbler flow and remove the flask. Rinse the Flask & Bubbler with a solution of 5% HCl + 5% H2O2 ***OR*** 10% HNO3 to remove traces of the SnCl2. Reassemble Reaction Flask and continue with other Standards till the table is complete & check the final curve.

[8] Use the Integrated Area of the Peak to establish a Calibration Curve, and interpolate Sample Peak Areas relative to this to get the appropriate concentrations.

[9] Be sure to rinse off the Bubbler assembly and the Reaction Flask well with DI Water and 2-5% Nitric Acid when finished to remove all traces of Reagents that may affect future analyses.

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