Vapor Generation Accessory VGA–77

Operation manual

Installation Category II
Pollution Degree 2
Safety Class 1 (EN61010-1)

VARIAN

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CE

Declaration of Conformity

We hereby Declare that the equipment listed below complies with the requirements of:
The Low Voltage Directive 73/23/EEC (93/68/EEC)

Applicable Standards

LVD BS EN 61010-1:1993
Equipment Model Number VGA-77 Vapor Generation Accessory

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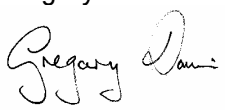
Signed: 
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Contents

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Safety practices and hazards

General

Operation of the VGA-77 with an Atomic Absorption spectrometer (AA), Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) or Inductively Coupled Plasma Mass Spectrometer (ICP-MS) involves the use of compressed gases and hazardous materials, including corrosive fluids. Unskilled, improper, or careless use of equipment can create explosion hazards, fire hazards or other hazards which can cause death, serious injury to personnel, or severe damage to equipment and property.

Appropriate safety practices have been included in this operation manual and your spectrometer operation manual, to help users operate the equipment safely. Read all safety practices thoroughly before attempting to operate your system.

If the equipment is used in a manner not specified by the manufacturer, the protection provided by the equipment may be impaired.

Hazard warnings

In addition to the hazard warnings contained in your spectrometer operation manual, specific hazard warnings have been included in this operation manual. These warnings state the hazard, describe how to avoid it and specify the possible consequences of not following the instructions. Read all warnings carefully and observe them at all times.

Electrical hazards

The VGA-77 contains electrical circuits, devices and components operating at dangerous voltages. Contact with these circuits, devices and components can cause death, serious injury or painful electric shock. Covers that are retained by screws on the VGA-77 may be opened only by Varian-trained, Varian-qualified or Varian-approved customer service representatives (CSR).

Use of the wrong supply voltage, connection of the accessory to an incorrectly wired supply outlet, or lack of proper electrical grounding can create a fire or shock hazard that can cause death, serious injury, or serious damage to equipment.

i. Always use a 3-wire outlet with a ground connection that is adequately rated for the load.

ii. The installation must comply with local, state and national safety regulations.

iii. Before connecting the VGA-77, make sure the voltage selector is correctly set for the mains supply to which you are connecting the accessory.

A blown fuse should be replaced with one of the same size and rating stated in the text near the fuse holder.

Chemical hazards

Vapor generation methods of analysis involve the generation of toxic hydrides and use materials which are toxic, highly corrosive or otherwise hazardous. Careless, improper, or unskilled use of such materials can cause serious personal injury.

Always ensure that laboratory safety practices governing the use, handling and disposal of such materials are strictly observed. These safety practices should include the wearing of appropriate safety clothing.

In the VGA-77 system, highly concentrated acids are pumped under pressure. If a leak occurs, acid could be sprayed from the system, causing serious personal injury. Always wear approved safety glasses warranted to protect the eyes.

Never pump concentrated sulfuric acid through the VGA-77 system.

Warning and Caution messages

A ‘Warning’ message is used in the text when failure to observe instructions or precautions could result in death or injury.

A ‘Caution’ message is used when failure to observe instructions could result in damage to equipment (Varian-supplied and/or associated equipment).

A ‘Note’ is used to give advice or information.

Triangular shapes indicate a warning on both the accessory and in this manual.

The following is a list of symbols that may appear in conjunction with warnings in the manual. The type of hazard they describe is also shown.

Electrical shock

Eye hazard

Noxious gases

Heavy weight (Danger to hands)

Hot surfaces

Fire hazard

Explosion hazard

Corrosive chemical

Moving part

Heavy weight (Danger to feet)

Toxic material

Sharp objects

Magnetic fields

Information symbols

I	Mains power on
0	Mains power off
	Fuse
	Single phase alternating current
CE	When attached to the rear of the instrument, indicates that the product complies with the requirements of one or more EU Directives.

Color coding

The various indicator lights appearing on the instrument and any associated accessories have been color coded to represent the status of the instrument or accessory:

- ❑ A green light indicates the instrument is in normal/standby condition.
- ❑ An orange light indicates that a potential hazard is present.
- ❑ A blue light indicates that operator intervention is required.
- ❑ A red light warns of danger or an emergency.

1. Introduction

1.1 About the VGA–77

The Vapor Generation Accessory 77 (VGA-77) is a vapor generation system for Atomic Absorption (AA), Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) applications.

Vapor generation is an extremely sensitive procedure used for determining the level of mercury, arsenic, selenium and a range of other hydride-forming elements. The sample capillary is placed in the solution to be measured and the VGA-77 pumps the sample through a reaction coil where it is automatically acidified and mixed with a suitable reductant. The resulting vapor is transferred to an atomization cell for determination by the spectrometer.

The VGA-77 is supplied in a modular form, with a pump unit and separate reagent module. Since ICP and AA applications use different gas/liquid separators, using separate plumbing assemblies for different reagents enables:

- ❏ Flexibility—the VGA-77 can be used with both AAs and ICPs
- ❏ Quick and simple change of applications, for example from AA to ICP or between different types of analyses
- ❏ Cleaner operation—there is no chance of cross-contamination between applications
- ❏ Ease of operation—there is no need to clean reagent bottles and tubing between applications as each application has a dedicated reagent module. Similarly, you can change from AA to ICP applications by changing reagent modules

Note Part numbers for additional reagent modules are listed in section 5.3.

1.2 About this manual

This manual includes instructions for installing, using and maintaining the VGA-77. You should use this manual in conjunction with your spectrometer operation manual and any other component or accessory manuals (for example a printer or sampler).

As you use this manual, there are some procedures that will apply to specific applications only. For example, the section referring to 'Installing the cell' does not apply if you are using your VGA-77 with a Varian ICP-OES or ICP-MS system. The instructions will inform you when this occurs.

1.3 Specifications

1.3.1 Environmental

Your accessory is designed for indoor use only. It is suitable for the categories stated on the front of this manual.

Condition	Altitude	Temp (°C)	Humidity (%RH) non-condensing
Non-operating (transport)	0-2133 m (0-7000')	5-45	20-80
Non-operating & meeting dielectric strength tests	sea level	40	90-95
Operating but not necessarily meeting performance spec's	0-2000 m (0-6562')	5-31 31-40	≤80 ≤{80-3.33(t-31)}
Operating within performance specifications	0-853 m (0-2800') 853-2133m (2800-7000')	10-35 10-25	8-80

1.3.2 Power

Information is correct at time of printing—information on the back of the accessory is the most up-to-date.

Voltage	100, 120, 220, or 240 volts AC ±10%, 230 +14% -6% volts AC, 230 +6% -14% volts AC.
Frequency	49-61 Hz
Consumption	approx. 20VA

Connections

Mains inlet coupler: 6A 250 VAC IEC type

Mains power cord connector:

Australia	10A 250 VAC	Complies with AS3112
USA	10A 125 VAC	Complies with NEMA 5-15P
Europe	6A 250 VAC	Complies with CEE7 sheet vii or NFC61.303VA

Fuses

T0.2A H250V, IEC 127 sheet 5, 5 x 20 mm (100-240 VAC)

Note For safety reasons, any other internal fuse or circuit breaker is not operator-accessible, and should only be replaced by Varian-authorized CSR.

Fuse information on the rear of the instrument is the most up to date.

1.3.3 Gas supplies

Argon or nitrogen, 99.99% pure (minimum)

The inert gas must be dry and dust-free, otherwise you must insert a suitable filter in the supply line.

Permissible pressure range	300 to 400 kPa (43 to 57 psi)
Recommended pressure	350 kPa (50 psi)
Normal flow rate	100 mL/minute

Gas connections, inert gas:
Inlet: 6 mm (1/4") ID reinforced PVC hose 3 metres long
Connectors

1.3.4 Weights and dimensions

Weight

Packed	11 kg (24 lb)
Unpacked	5.5 kg (12 lb)

Dimensions (W x D x H)

Packed	590 x 475 x 320 mm (23 x 19 x 13 in)
Unpacked	320 x 210 x 270 mm (13 x 8 x 11 in)

2. Getting started

2.1 Unpacking

Open the shipping case and the enclosed packages with care. Inspect all parts for damage in transit. Any damage should be reported immediately.

You should have received the following:

- ❑ The VGA-77 pump unit
- ❑ A cover for the pump unit
- ❑ A drip tray for the pump unit
- ❑ A reagent module with two reagent bottles
- ❑ Two quartz cells with a length of black Fluoro-elastomer tubing (AA only)
- ❑ Power cable
- ❑ Tubing and connectors kit and spare 6 mm ID hose (used to connect a mercury trap)
- ❑ Clear tubing (10 mm ID)
- ❑ Hose clamp and fuses
- ❑ Cell holder for Mark 7 burner (AA only)
- ❑ This operation manual.

Note Spare parts and their part numbers are given in section 5.3.

2.2 Installation

Before proceeding with the installation, you should read the ‘Safety practices and hazards’ section at the start of this manual. You should also be completely familiar with the safety procedures required for operation of your spectrometer.

You should refer to the diagram below during installation to help you identify the different parts of your VGA and pump module.

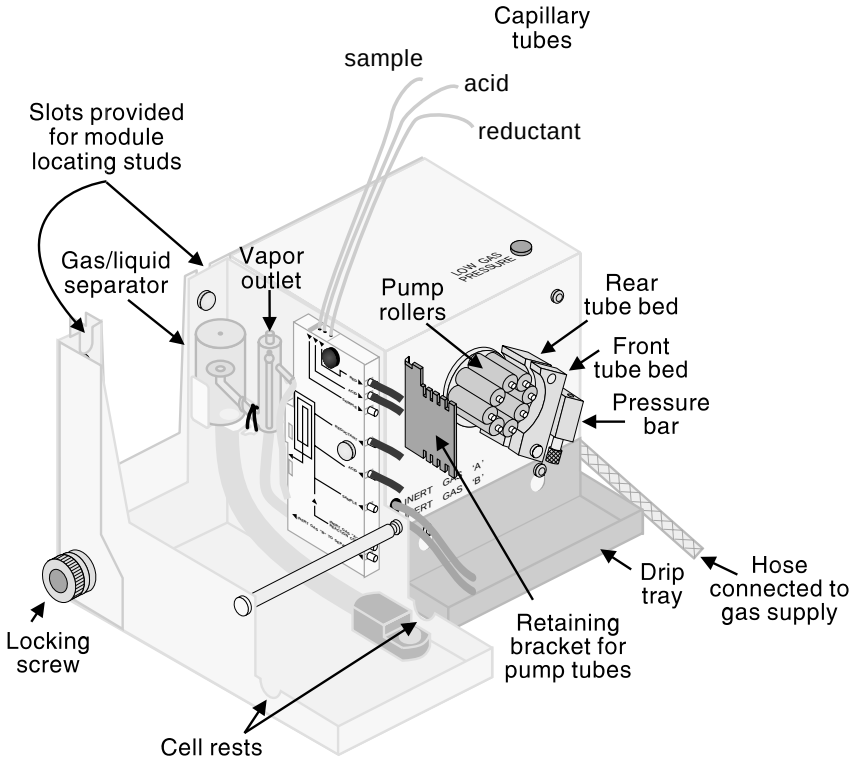

Figure 1. VGA-77 with AA module installed

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2.2.1 Installation checklist

Use the following checklist to help you complete each step of the installation.

- ❑ Check that the correct gas supply is available, then connect your VGA-77 to the supply.
  Refer to section 2.2.2.
- ❑ Check that the correct power supply is available, the correct fuses are installed and that the voltage selector is correctly set.
  Refer to section 2.2.3.
- ❑ Check the environmental requirements.
  Refer to section 1.3.1.
- ❑ Install the pump unit.
  Refer to section0.
- ❑ Install the reagent module.
  Refer to section 0.
- ❑ Install the drain tubing.
  Refer to section 2.2.6.
- ❑ Install the VGA pump tubing.
  Refer to section 2.2.7.

AA only:

- ❑ Install the burner clamps.
  Refer to section 2.2.8.
- ❑ Install the cell.
  Refer to section2.2.10.

- ❑ Connect the gas/liquid separator outlet to:
  the inlet of the absorption cell (AA), or
  the sample introduction system (ICP).
  Refer to section 2.2.11
- ❑ If necessary, connect a mercury trap to the cell exhaust to comply with local regulations on the discharge of mercury vapor (AA only).
  Refer to section 0.

2.2.2 Gas supply requirements

A regulated supply of argon must be provided for your VGA-77 through the captive hose located in the right-hand side panel. You may also use nitrogen with the AA reagent module only.

Note Nitrogen must not be used with the ICP module as it may degrade the performance of the plasma.

The gas supply must comply with the specifications in chapter 1. The VGA is fitted with a 6 mm (1/4") internal diameter reinforced plastic hose for connection to a standard barbed-tail connector. If you are in any doubt about the correct fittings to use, consult your supplier.

Connecting the gas supply

To connect the gas supply:

1. Place the clamp over the free end of the captive hose and connect the free end of the captive hose to the metal barbed-tail connector on the gas supply or to your gas supply regulator.
2. Tighten the clamp, by adjusting the screw, to secure the gas supply hose to the gas supply. Adjust the pressure at the regulator to the recommended pressure.

Caution The argon supply pressure supplied to the VGA-77 must be 300 to 400 kPa (43 to 57 psi).

☆☆☆ *Hot Tip* *The VGA-77 gas supply may be taken from the main argon gas line to ICP spectrometers if you use the following precautions:*
Insert a suitable 'T' piece into the main argon gas supply to divert some of the gas to the VGA.
Attach a regulator to control the flow of argon to the VGA. Place a tap in the argon supply to the VGA. The tap is required to shut off the argon supply to the vapor generator, as gas will flow through the VGA-77 even when it is switched off.

Within the VGA-77, the inert gas supply is divided into two branches. The first branch is controlled by a solenoid stop valve. It supplies gas to the inlet side of the reaction coil. The second branch supplies inert gas directly through the gas/liquid separator.

Note Inert gas will flow through the separator even with the VGA-77 switched off. When the VGA-77 is switched on, it will flow through both branches. To reduce gas consumption when the VGA is not in use, a shut-off valve in the inlet gas supply is recommended. The gas supply can then be shut off when the VGA is switched off.

During operation, the gas supply pressure is automatically monitored by a built-in sensor. If the gas supply is interrupted, or if the supply pressure falls below the specified minimum, the indicator light will be illuminated, and the gas supply to the reaction coil is shut off. Operator intervention is required to fix the low gas pressure.

The indicator light is the single blue light on the top panel of the accessory. If the indicator light turns on, switch the VGA-77 off immediately, rectify the gas supply problem, then switch the VGA-77 back on. If the indicator light again turns on, you should call your Varian CSR.

2.2.3 Power supply requirements

The voltage selector, mains receptacle, power switch and fuses are located on the right-hand side of the accessory.

Before connecting the mains power for the first time, check that the correct power supply is available, the voltage selector switches on the accessory are set correctly, and that the correct fuses are installed and both fuses are of the same rating.

Warning
Application of the wrong supply voltage, connection of the accessory to an incorrectly wired supply outlet, or lack of proper electrical grounding can create a fire or shock hazard that can cause death, serious injury or serious damage to equipment.

For power supply and fuse specifications refer to the ‘Specifications’ section in chapter 1 of this manual. Refer to the fuses section in the Maintenance chapter of this manual for details of how to inspect and replace fuses.

Selecting the voltage

Refer to the table immediately above the selector switches or consult the following table and set the switches as required. For example, if the accessory is connected to 240 volts, the table tells you that the switch setting should be ‘AD’. This means the left switch should be up (position ‘A’) and the right switch should be down (position ‘D’).

Voltage	Switch setting	Switch positions	
		left	right
240 ± 10%	AD	Up	Down
230 +14% -6%	AD	Up	Down
230 +6% -14%	BD	Down	Down
220 ± 10%	BD	Down	Down
120 ± 10%	AC	Up	Up
100 ± 10%	BC	Down	Up

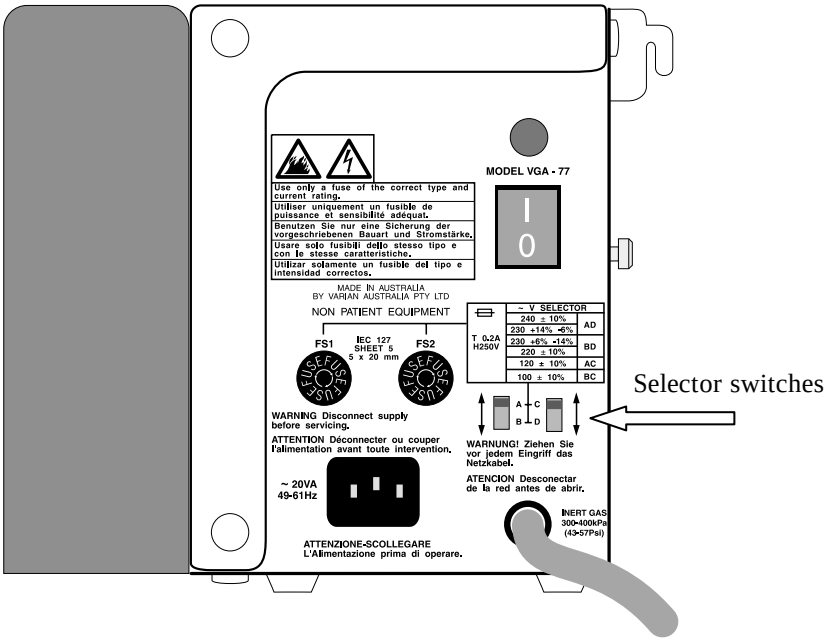

Figure 2. Side of the VGA-77

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2.2.4 Installing the pump unit

To install the VGA-77 on a Varian AA, insert the hooks on the back of the unit into the slots located on either side of the Varian AA sample compartment.

For an instrument other than a Varian AA, you should place the VGA-77 flat on a bench, close to the sample compartment of the instrument.

When the VGA-77 is in position, fit the drip tray to the front of the pump unit by positioning the large holes over the studs on the front of the VGA-77 and sliding the tray downwards.

2.2.5 Installing a reagent module

To install a reagent module into the VGA-77:

1. Loosen the locking screw at the lower rear left hand corner of the pump unit.
2. Lower the reagent module into the space adjacent to the left-hand side of the pump unit, ensuring the reagent module locating studs are fully home in the slots.
3. Wind the locking screw in until it holds the module firmly in place.
4. Fit the end of the tube from the pump unit marked ‘Inert gas ‘A’’, (the top tube on the front of the VGA), to the nipple near the bottom of the reagent manifold marked ‘Inert gas ‘A’ to reaction coil’. The nipple has a contoured profile. Push the tubing onto the nipple until it covers all of the contoured section.

Figure 3 Fitting the tubing.

5. Fit the end of the tube from the pump unit marked ‘Inert gas ‘B’’ to the nipple near the bottom of the reagent manifold marked ‘Inert gas ‘B’ to separator’. The nipple has a contoured profile. Push the tubing onto the nipple until it covers all of the contoured section.

Note To remove a module and replace it with another, refer to the instructions in section 3.5.

2.2.6 Installing the drain tubing

Warning
Waste solutions from the VGA-77 may contain concentrated acids which can cause severe burns. Your waste vessel must be of durable, acid-resistant material. Do not use a glass container. Locate the vessel where it cannot be knocked over. Empty it frequently. Dispose of waste solutions in accordance with relevant safety practices.

There are two drain outlets located on the underneath side of the reagent module. The outlet closest to the front face of the module is for tray overflow, the other is to drain liquid from the gas/liquid separator.

Figure 4. Drain outlets

Drain tubing should be connected to both of these drain outlets. To connect drain tubing to the drain outlet, push the tubing over the outlet hole so that the wall of the tubing seats firmly into the cavity surrounding the outlet hole.

AA

1. Cut a suitable length of the plastic drain tubing supplied with your reagent module.
2. Connect one end of the tubing to the large outlet underneath the module tray. The tubing should be connected between the inner and outer rings on the outlet. Place the free end in your waste vessel. Ensure that the tubing is free of kinks or sharp bends so that the waste liquid will drain freely into the waste vessel.

Note The end of the tube must be above the surface of the liquid. If the end of the drain tube is submerged, possible back-pressure may lead to unreliable results.

ICP

1. Fit a purple-black pump tube to the instrument peristaltic pump as described in your instrument operation manual.
2. Connect the inlet of the purple-black pump tube to the drain outlet of the gas/liquid separator in the ICP reagent module. (Refer to section 2.2.11 for a diagram of the ICP plasma gas/liquid separator.)
3. Attach a suitable length of the Nalgene tubing supplied to the outlet of the purple-black pump tube from the ICP instrument. Place the free end of the Nalgene tubing into the waste container. Ensure that the tubing is free of kinks or sharp bends so that the waste liquid will drain freely into the waste vessel.

Note Use only the purple-black tubing for draining the ICP/VGA-77 system. Other pump tubing, for example the black-black tubing, may not give a large enough drain flow rate. The instrument peristaltic pump rate must be sufficient to remove all waste liquid from the gas/liquid separator. (Typically 40 – 45 rpm.)

2.2.7 Installing the VGA-77 pump tubing

1. Open the pressure bar to release the front and rear tube beds. Swing both tube beds clear of the pump rollers.
2. Fit black-black tubing into the two innermost tubing slots and purple-black tubing to the outer most tubing.

3. Connect the inlet end of the innermost tube to the black rubber connector at the top of the reagent manifold marked ‘Red. ->’. Connect the other end to the black rubber connector near the middle of the reagent manifold marked ‘Reductant <-’.
4. Connect the inlet end of the middle tube to the black rubber connector at the top of the reagent manifold marked ‘Acid ->’. Connect the other end to the black rubber connector near the middle of the reagent manifold marked ‘Acid <-’.
5. Connect the inlet end of the outer tube to the nipple at the top of the reagent manifold marked ‘Sample ->’. Connect the other end to the nipple near the middle of the reagent manifold marked ‘Sample <-’.The nipples have a contoured profile. Ensure the tube is pushed all the way home and covers all of the contoured section of the nipple.
6. Swing the rear tube bed against the rear tubes and ensure that:
   i. The bed bears evenly against the tubes
   ii. The tubes are seated squarely on the pump rollers.
7. Adjust the position of the tubes if necessary.
8. Repeat step 9 with the front tube bed.

☆☆☆ *Hot Tip* *If you shorten the ‘tails’ of the pump tubing, you may reduce reagent and sample volume in the tubing, thereby reducing sample consumption and reducing pre-read delays.*

☆☆☆ *Hot Tip* *The mixing coil is particularly required for mercury analysis. Analysis times for hydride elements can be reduced by using a shorter length of the mixing coil tubing. A separate module could be dedicated to this application.*

2.2.8 Installing the burner clamp

This section applies to AA modules only.

Caution Do not use the cell with a nitrous oxide–acetylene burner. The cell will be destroyed if exposed to a nitrous oxide-acetylene flame

Mark 7 burner

The VGA-77 is supplied with a cell holder for the Mark 7 burner. The Mark 7 does not require mounting brackets as the cell holder simply sits on top of the burner.

Figure 5. Mark 7 burner without holder

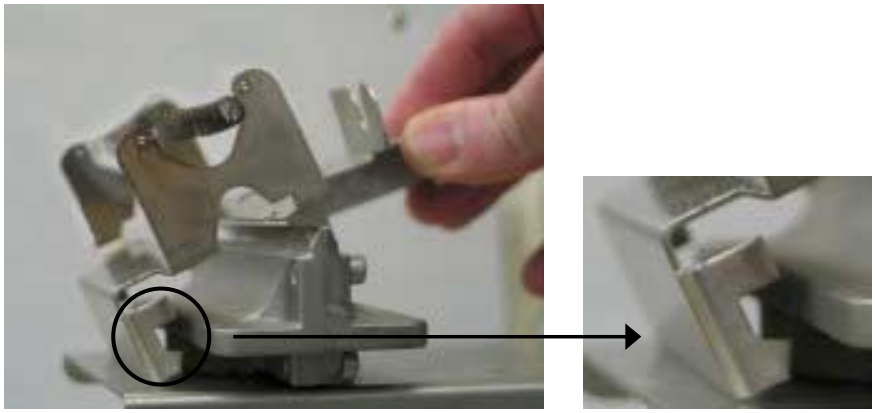

Figure 6. *Seat cut-outs of the holder over the back edge of the burner. Close up view of the cut outs.*

Figure 7. Pull the holder forward so that the cut-outs hook around the burner edge.

Figure 8. Lower the holder into position.

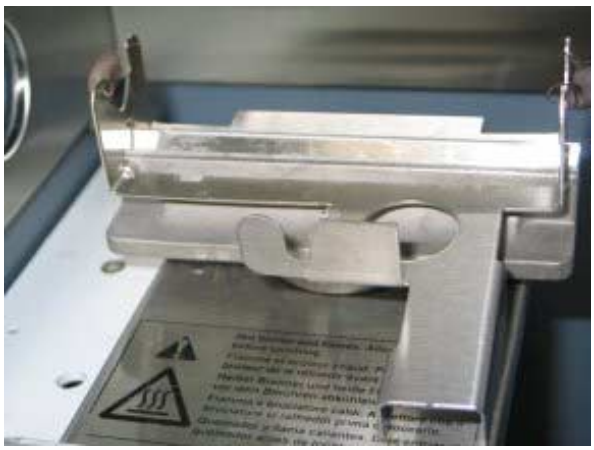

Figure 9. Mark 7 burner with holder in position

Mark VI and VI–A burners

If you have a Mark VI or Mark VI-A burner, you will need a cell holder and suitable mounting brackets for these burners. (Refer to section 6 for ordering information.)

To install these mounting brackets on the burner, use the following procedure:

1. Align the burner clamps at either end of the burner, with the mounting peg pointing inward and the hole in the end of the plate aligned over the hole in the end of the burner.
2. Use the screws provided to fix the burner clamps in position.

Note The clamps can be left permanently installed since they will not interfere with normal flame analyses.

Figure 10. Mark VI burner with burner clamps installed

Note The Mark VI-A burner looks different to the Mark VI burner, however the procedure for installing the clamps is the same.

Mark V burner

If you have a Mark V burner (or earlier version), you will need a cell holder and burner mount for this burner. (Refer to section 6 for ordering information.)

To install the burner clamp for the Mark V burner, refer to the picture below and use the following procedure:

1. Slacken the two clamping screws on the underside of the clamp.
2. Note that the ‘front’ of the air-acetylene burner carries the identification label. Orient the clamp so that the two mounting pegs are at the front of the burner. This will ensure that the burner identification label is still visible through the ‘open’ portion of the clamp.
3. Fit the clamp over the burner so that the two positioning lugs at each end of the clamp rest on top of the burner, on either side of the burner slot.
4. Tighten the clamping screws.

The clamp can be left permanently installed since it will not interfere with normal flame analyses.

Figure 11. Mark V burner with burner clamps installed

2.2.9 Installation of Zeeman adapter—AA240 Z and AA280 Z

The VGA for Zeeman Adapter allows the VGA to be used with the Varian AA240Z/AA280 Z The Adapter allows installation of the following cells in the sample compartment:

- Mercury flow-through cell
- Standard hydride absorption cell
- ETC-60 Cell Mk 2

Assembly

The following instructions outline the steps required to assemble and change cell holders of the VGA for Zeeman Adapter. When assembled the Adapter is hooked over the sample compartment.

The VGA for Zeeman Adapter is shipped with the Standard Cell Holder and a bracket for the ETC-60 Workhead Mk 2.

Figure 12. Standard cell holder (rear view)

Figure 13. Bracket for the ETC-60 workhead

Adapter and Standard Cell Holder installation

Note It is necessary to remove the Zeeman workhead to install the Adapter.

To install the Adapter:

1. Remove the sampler and the Zeeman workhead from the instrument (refer to your sampler and instrument manuals for detailed instructions).

Warning
The workhead weighs approximately 16 kg (35 lbs). To avoid injury or damage always handle carefully.

Note The VGA-77 can be fitted to the front of the instrument as described in the instrument operation manual.

2. Make sure that the sample compartment is empty

Note Now is a good time to develop a method and align the lamps.

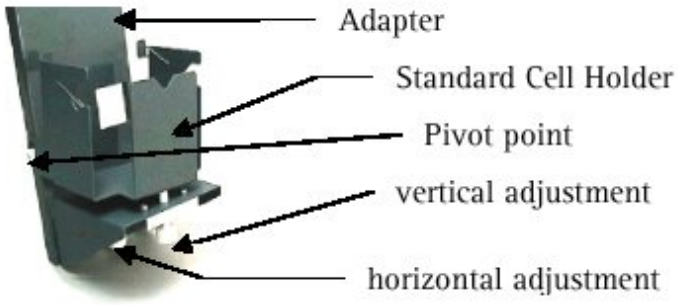

Figure 14. Adapter and Standard Cell Holder

3. Attach the Standard Cell Holder to the Adapter outside the sample compartment. Lower the hooks of the Standard Cell Holder onto the pivot points of the Adapter.
4. Pass the Adapter fitted with the Standard Cell Holder under the crossbar of the sample compartment.
5. Hook the Adapter on the top rear edge of the sample compartment

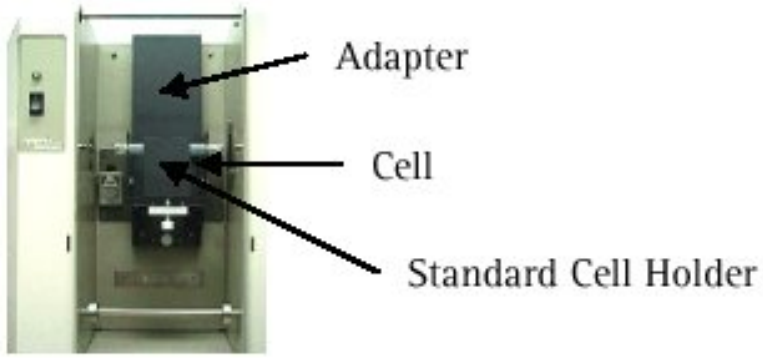

Figure 15. Adapter, Standard Cell Holder and Cell inside sample compartment

Cell Holder and Adapter removal

The standard cell holder must be removed to allow installation of the bracket for the ETC-60 workhead Mk 2.

1. Lift the cell holder up to unhook the cell holder from the Adapter mounting.
2. Lift the Adapter out of the sample compartment, carefully avoiding the crossbar.

2.2.10 Installing the cell

This section applies to AA modules only.

Note While acceptable results for mercury can be obtained with the standard absorption cell, Varian's flow-through mercury cell is recommended, since this will generally provide better analytical sensitivity and precision.

Note Also, for locations where the discharge of mercury vapor in nanogram quantities is not permitted, the standard absorption cell is not suitable. In these locations you should use the flow-through mercury cell together with a suitable trap (see section 2.2.12).

Warning
Absorption cells are fragile. Handle with care.

Installing a standard absorption cell on a Mark 7 burner

To install a standard absorption cell on a Mark 7 burner, do the following:

1. Lift the left hand spring and pass the left hand side of the cell through the cut out in the mounting bracket.
2. Gently release the left hand spring.
3. Lift the right hand spring, gently push the cell fully home and gently release the right hand spring. The cell should be positioned as shown in the diagram above.
4. Position the central inlet stem in the cell holder slot.

Figure 16. Mark 7 burner with standard absorption cell in cell holder positioned on top

Installing a flow-through mercury cell on a Mark 7 burner

To install a flow-through mercury cell (for mercury analysis) in a Mark 7, use the following procedure:

1. Open the spring clips and place the cell into position.
2. Close the spring clips.
3. Place the cell in its holder on top of the burner.

Installing a standard absorption cell on older burners

To install a standard absorption cell on older burners (e.g., Mark VI, Mark VIA, Mark V), use the following procedure:

1. Lift the left hand spring clip, and pass the central inlet stem through the hole in the mounting bracket while lowering the left side of the cell into position.
2. Close the left hand spring clip.
3. Open the right hand spring clip, gently push the cell fully home and close the right hand spring clip.
4. Mount the cell in its holder on the burner. Note that the slots on the cell holder must engage the mounting pegs on the burner clamp.

Installing a flow-through mercury cell on older burners

To install a flow-through mercury cell (for mercury analysis) on older burners (e.g., Mark VI, Mark VIA, Mark V), usedo the following procedure:

1. Open the spring clips and place the cell into position.
2. Close the spring clips.
3. Mount the cell in its holder on the burner. Note that the slots on the cell holder must engage the mounting pegs on the burner clamp.

2.2.11 Connecting the gas/liquid separator outlet

The VGA-77 is supplied with a length of black fluoro-elastomer tubing (AA only). This tubing is used to connect the vapor outlet of the gas-liquid separator to the inlet stem of the quartz absorption cell.

It is good analytical practice to keep this tubing as short as possible. Your VGA-77 should be located immediately in front of the instrument sample compartment.

AA module

If you are using the AA reagent module, you should connect the outlet of the gas/liquid separator to the inlet of the cell as follows:

1. Use a sharp scalpel to neatly cut an appropriate length of the black fluoro-elastomer tubing supplied.
2. Fit one end of the tubing over the inlet stem of the cell (for Hg cell push tubing into the inlet) and the other end over the vapor outlet of the gas/liquid separator.

When the VGA-77 is not being used, disconnect the tubing from the separator and store the cell in its holder at the front of the module.

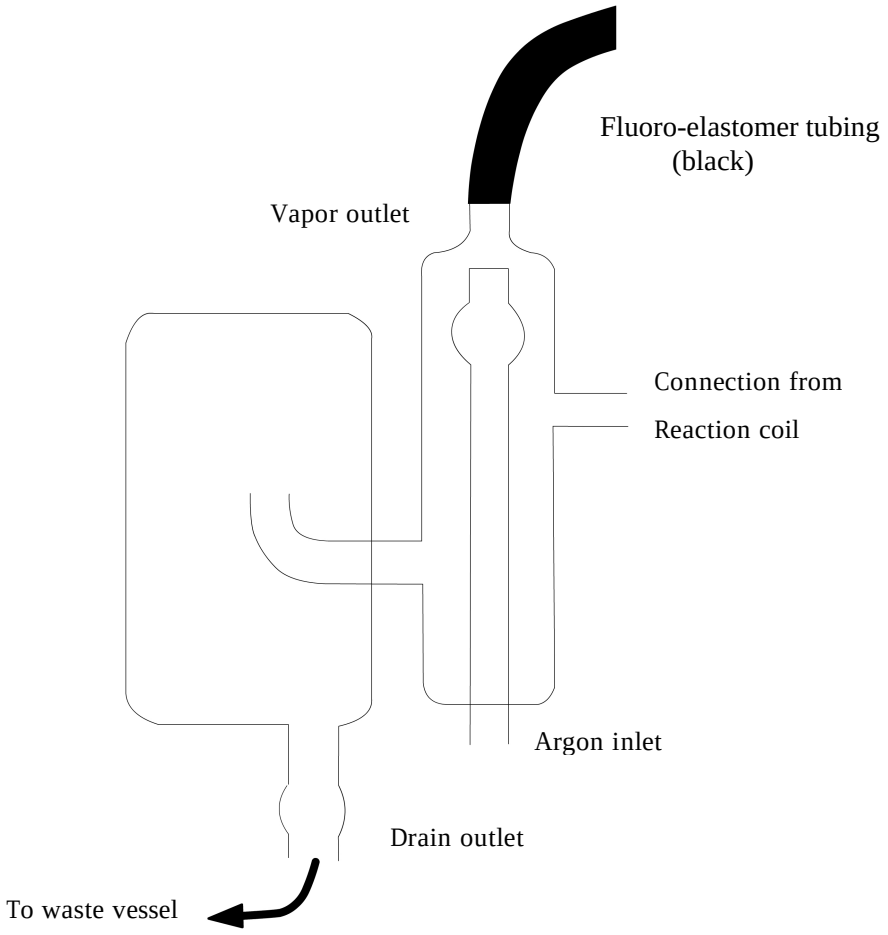

Figure 17. Gas/liquid separator for an AA module

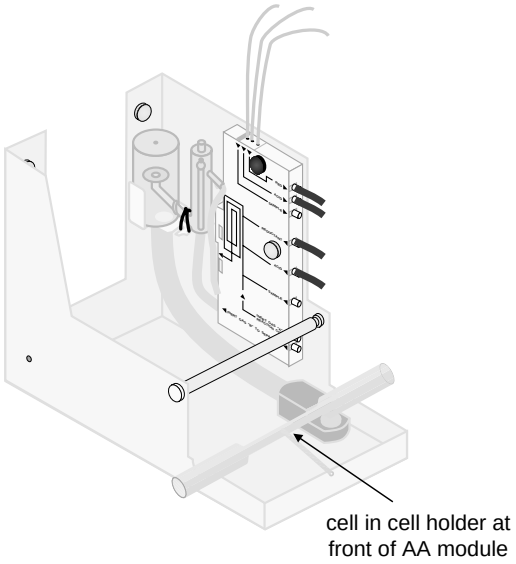

Figure 18. Cell resting in module holder, when not in use

ICP module

If you are using the ICP reagent module, follow the steps below to connect the plasma gas/liquid separator outlet to the ICP instrument.

Note It is possible to connect the vapor generator to the ICP-OES or ICP-MS systems while the plasma is on.

1. Set up the sample introduction system as described in the ICP operation manual.
2. Use a sharp scalpel to neatly cut a length (appropriate to your installation) of the black fluoro-elastomer tubing supplied.
3. Fit the large black fluoro-elastomer tubing over the vapor outlet of the plasma gas/liquid separator.
4. Measure the minimum length of the supplied polyethylene tubing required to connect the free end of the black fluoro-elastomer tubing to the sample inlet of the ICP nebulizer. Neatly cut the required length and make the connection.

☆☆☆ *Hot Tip* *For mercury determinations using $SnCl_2$, the drain peristaltic pump tubing from the spectrometer should be pinched to prevent loss of gaseous mercury through the pumped drain.*

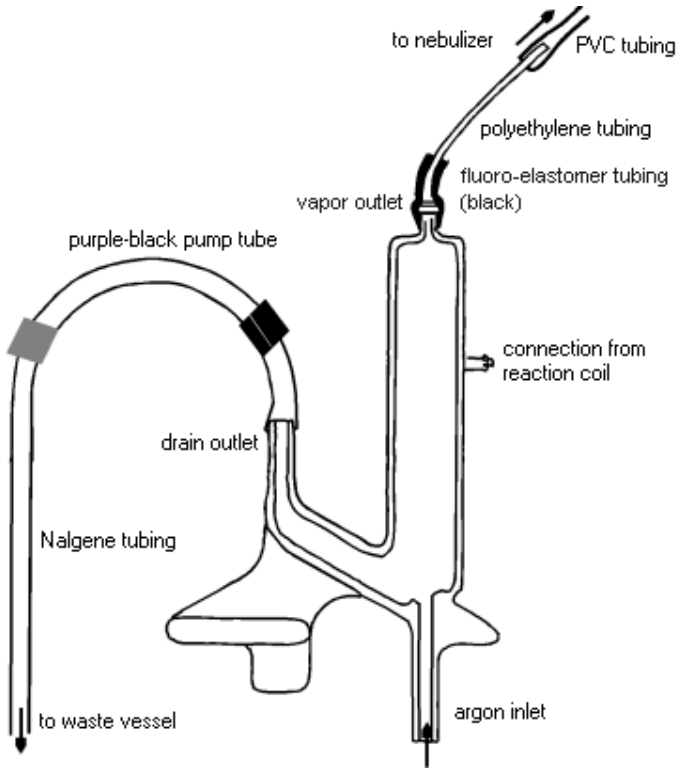

Figure 19. Plasma gas/liquid separator for ICP module

2.2.12 Connecting a mercury trap

You should use a sharp scalpel to cut two suitable lengths of the supplied 6 mm diameter clear PVC tubing, and connect them to the two cell ports. Connect the free ends to the outlet and then to a suitable mercury trap in accordance with local regulations governing the discharge of mercury vapor.

☆☆☆ *Hot Tip* *Fitting is easier if the ends of the tubing are first softened in hot water.*

Caution

Bubble type collectors must not be used, because the VGA-77 is not designed to accommodate the excessive back pressure generated by such collectors. Using bubble type collectors may lead to vapor being forced through the drain of the gas/liquid separator and results in an unreliable signal.
Collectors of loosely packed metal foil may be suitable if they comply with local laws

2.2.13 Connection to the Autosampler

The VGA-77 may be connected to a Varian or compatible autosampler for automatic sampling. Use a suitable piece of tubing to join the sample capillary on the VGA-77 to the Teflon tubing attached to the probe of the autosampler.

3. Operation

Warning
Vapor generation methods of analysis involve the generation of toxic hydrides and require the use of materials which are toxic, highly corrosive or otherwise hazardous. Careless, improper, or unskilled use of such materials can cause serious personal injury. Always ensure that laboratory safety practices governing the use, handling and disposal of such materials are strictly observed. These safety practices should include the wearing of appropriate safety clothing.
In the VGA-77 system, highly concentrated acids are being pumped under pressure. If a leak occurs, acid could be sprayed from the system and cause serious personal injury. Always wear approved safety glasses warranted to protect the eyes.
Never pump concentrated sulfuric acid through the VGA-77 system.

In the VGA-77 system, the vapor is generated continuously while solutions are being pumped. This provides the convenience and advantages of a continuous analytical signal.

3.1 Setup

3.1.1 General setup

1. Check you have the correct module installed.
2. Ensure that the inert gas supply to the VGA-77 is on, with the cylinder regulator set to the recommended pressure of 350 kPa (50 psi).
3. Ensure that the peristaltic pump is adjusted correctly as detailed in section 3.1.2 below.
4. Set up any other accessories you require (for example, printers or samplers) according to their instruction manuals.
5. Set the instrument parameters for the element to be determined.

Use the integration mode with Varian AA or ICP-OES systems. (Varian AA users can also use PROMT mode.)
ICP-MS users should select the Peak hopping mode with a Dwell time of around 400 µs and 50-100 scans per replicate.

6. Fill the reagent container(s) with the required reagent(s). (Refer to chapter 4.)

3.1.2 Pump adjustment

1. Set the regulator to the recommended pressure and turn on the inert gas supply.

Note Ensure that the inert gas supply is turned on before switching on the VGA-77 power. If you start to pump solutions through the system before the inert gas is turned on, the signal will be unreliable.

2. Select the appropriate power lead, and connect the VGA-77 to the mains power supply.
3. Place the three capillary tubes in a container of distilled water and switch the VGA-77 on. The green 'Power' indicator light is illuminated when the power is on. Note that the peristaltic pump will run continuously once the power is switched on.
4. Slacken both pressure adjusting screws. Swing both tube beds against the pump tubing and close the pressure bar.
5. Slowly tighten the front (sample) pressure adjusting screw until water is obviously being pumped through the tube. Tighten the pressure adjusting screw a further half turn. At this setting the pumping rate will be close to optimum. Any further tightening of the screw will tend to reduce the pumping rate.

Caution Do not over-tighten the pressure adjusting screws. Excessive tightening will shorten the life of the pump tubes and could cause permanent damage to the pump.

✎ Note At this stage, inert gas may be seen bubbling out of both the other tubes. This is a normal consequence of pressurizing the system and this situation is automatically corrected when you adjust the clamp pressure for these tubes.

☆☆☆ *Hot Tip* *To see if the liquid is being pumped smoothly, you can deliberately create air bubbles by dipping the capillary in and out of the container.*

6. Repeat step 5 with the rear pressure adjusting screw.
7. Measure the uptake rate through the sample pump tubes. You can do this by filling a suitable measuring cylinder to a convenient reference mark with distilled water, then placing the sample capillary into the cylinder and observing the volume of water pumped out of the cylinder over a timed interval.

   The uptake rate should be within the range 6-8 mL/min. Note the exact flow rate for future reference in the AA performance log in appendix A at the rear of this manual.
8. Similarly measure the uptake rate for each of the other pump tubes. The uptake rate for each should be within the range 0.8-1.2 mL/min. Note the exact flow rates for future reference in the AA performance log in appendix A at the rear of this manual.
9. If you are using the VGA-77 with an ICP system, you must now adjust the speed of the instrument peristaltic pump until liquid is being pumped out of the gas/liquid separator faster than it is being pumped in by the VGA-77. Set the spectrometer **Pump speed** to a minimum of 35 rpm.

Your VGA-77 is now ready for use. You should now either:

- ❏ Proceed to section 3.1.3, if you are using the VGA-77 with an AA system
- ❏ Proceed to section 3.1.4, if you are using the VGA-77 with an ICP system, or
- ❏ Carry out the instructions for closing down the VGA-77 given in section 3.4.

3.1.3 AA setup

1. Remove the cell in its holder from the burner and place it at the front of the reagent module.
2. Lower the burner using the burner height controls so that it is clear of the optical path.

Note Varian recommends using reduced slit height (0.5) in all methods.

3. Fit the required hollow cathode lamp and set up the spectrometer as described in your instrument operation manual.
4. Select Optimize, then Optimize Lamp.
5. Position the cell in its holder on top of the burner.
6. Align the cell in the optical path as follows:
   i. Hold a piece of white card between the right-hand end of the absorption cell and the sample compartment window.
   ii. Using the burner positioning controls, adjust the position of the cell until the light from the hollow cathode lamp passes through the cell onto the card. Remove the card.
   iii. Use the burner positioning controls to adjust the position of the cell for maximum transmission.

For mercury determinations, proceed to 'Conditioning the system'.

Lighting the flame

1. Carry out any safety checks described in your spectrometer operation manual. Follow all instructions and observe all warnings.
2. Set the acetylene flow rather higher than normal in order to obtain a fuel-rich air-acetylene flame, this is required for the igniting the flame.

Note Some instruments may automatically set a fuel-rich mixture. You should refer to your spectrometer operation manual for details.

Warning
With the VGA-77 cell installed, the burner will be lower than usual, and a standard mixture or a fuel-lean mixture may not ignite readily. To avoid an explosive accumulation of fuel and oxidant in the sample compartment, ALWAYS ensure that the gas mixture is fuel-rich before operating the Ignite button.

3. If a Mark VI burner is fitted, tilt the absorption cell clear of the burner. (On older instruments this will also ensure that the igniter arm does not strike the cell.)

Caution — If you leave the absorption cell in a fuel-rich flame, carbon particles may be deposited on the outside wall of the cell. Under these conditions, the cell can be permanently damaged by local overheating

4. Ignite the flame and adjust the fuel flow to give a lean flame. If necessary (as is the case with older instruments) lower the cell back to its normal position.

Conditioning the system

The objective of this procedure is to 'condition' the complete system and obtain a stable signal before calibrating the instrument and analyzing your samples.

This procedure should be carried out:

- ❑ When the system is first installed
- ❑ After the system has been completely flushed and cleaned
- ❑ When a new absorption cell (or flow-through mercury cell) is fitted
- ❑ Whenever new pump tubes are fitted
- ❑ When the reaction coil is renewed.

1. Allow the pump to operate for three or four minutes to stabilize the flow rates.
2. Make sure the instrument is in 'Abs' mode with a suitably short integration period.
3. Aspirate your highest standard, monitor the signal, and note the time interval for the signal to rise from zero to its stable value. The time that you measure will be the pre-read delay you should enter into your system software.

Note — When presenting solutions to the system, always wait until this period has elapsed before taking a reading.

4. Aspirate your analytical blank.
5. Continue to aspirate the standard and analytical blank in turn until a consistent response is obtained for the standard solution, then proceed to section 3.2.

If a consistent response cannot be obtained within a reasonable time, contamination is the likely cause. Even slight contamination of the system can suppress production of hydride (or mercury vapor). In this circumstance, you must suspend the conditioning procedure and clean the system thoroughly before continuing. Refer to section 5.1 for cleaning instructions.

Note A consistent response refers to obtaining a repeatable and consistent absorbance reading.

3.1.4 ICP setup

The following procedure conditions the ICP system for the vapor generation analysis. This procedure should be carried out:

- ❏ When the system is first installed
- ❏ After the system has been completely flushed and cleaned
- ❏ When new pump tubes are fitted
- ❏ When the reaction coil is renewed
- ❏ Before each analysis.

1. Ensure that the plasma is on and the peristaltic pump is operating.
2. Allow the pump to operate for three or four minutes to stabilize the flow rates.
3. Perform a time scan on the Time Display page of Liberty and Vista systems or in the Time Scan window of ICP-MS system. View the signal as you alternate between the blank and top calibration standard. Use the cursor to determine the suitable delay time required.

Note Due to the high sensitivity of the VGA-77/ICP-OES system, the upper concentration of standards used for calibration is limited (by memory effects etc.). For hydride forming elements, use a top standard of about 100 ppb. For ICP-MS a lower top standard concentration of not more than 10 ppb is recommended.

4. Continue the previous step until a consistent response is obtained. When the response is consistent, the system is ready for use. Remember to optimize the operating conditions for your program. Pay particular attention to sample delay, stabilization and rinse times.

If a consistent response cannot be obtained within a reasonable time, contamination is the likely cause. Even slight contamination of the system can suppress production of hydride (or mercury vapor). If this happens, stop the conditioning procedure and clean the system thoroughly before continuing. Refer to section 5.1 for VGA cleaning instructions, and refer to your instrument manual for details on cleaning your ICP.

3.2 Operation

Before starting the analytical program you must measure the analytical signal caused by the presence of analyte in:

- ❑ The acid and reductant solutions being pumped through the system
- ❑ The analytical blank solution.

To do this:

1. Place all three uptake tubes in a single container of distilled water. Wait for about 40 seconds to allow the system to stabilize. Perform an instrument zero.
2. Leave the sample uptake tube in distilled water and place the acid and reductant uptake tubes in their respective reagent solutions. Wait for about 40 seconds and measure the absorbance. Any absorbance registered is attributable to analyte in the solutions being pumped through the system.
3. Place the sample uptake tube in the analytical blank solution. Wait for about 40 seconds and measure the absorbance. This measurement is the total absorbance attributable to analyte in all solutions used (acid, reductant, analytical blank).
4. The measurements obtained in the previous two steps allow you to decide whether the blank signal is acceptable or not before using the blank solution to calibrate the instrument at analytical zero.

You can now calibrate the system and measure your samples.

Samples can be presented to the system manually by dipping the sample capillary tube into a flask, test tube or vial. You can use the VGA-77 with non-Varian instruments and samplers.

The general procedure for using automatic samplers is given in the next section.

3.3 Automatic operation

Caution — Operation of the VGA-77 is not interlocked to the system. In the event of gas supply failure, pumping faults, or if the reagent containers are emptied, the program will not be automatically stopped and results from the program will not be analytically valid.

Observe the following general rules, but refer to the appropriate instrument operation or system manual for specific operating instructions.

- ❑ The VGA-77 technique requires the use of acids at high concentrations. You must therefore ensure that the sample probe on the autosampler is corrosion-resistant. The Varian SPS2/3 and SPS-5 are fitted with a corrosion-resistant probe. This probe should always be used for VGA-77 applications.
- ❑ When connecting the autosampler to the VGA-77 uptake capillary, ensure that the joint is leak-free and offers minimal dead volume by keeping the connecting tube as short as possible. The uptake from the autosampler to the vapor generator is the only connection required between VGA-77 and other system components—no electrical interconnection is required.
- ❑ Remember to enter a suitable delay time to allow for the extra time needed for the solution to emerge from the autosampler tubing. Also check the stabilization times.
- ❑ In the software, select the required number of replicate measurements to be taken and select the appropriate re-calibration and reslope frequencies.

Note — At the end of an automatic run the VGA pump continues to run and gas continues to flow. To avoid waste liquid flooding the system, set the ‘Pump rate at end of sequence’ in the Preferences page to a rate that ensures the removal of all waste liquid from the gas/liquid separator. (Typically 40 – 45 rpm.)

- ❑ Load the autosampler with your analytical blank, standard solutions and samples in the correct locations.

- ❑ Save your revised method.
- ❑ Before starting the analytical program, carefully check all sampling parameters to ensure that they are correct. Also check that the reagent containers are full.

3.4 Shutting down

1. Turn off the flame/torch as described in your instrument's operation manual. Leave the VGA-77 switched on. You will also need to leave the ICP pump running.
2. Run a concentrated hydrocholoric acid solution through the system for 2 to 5 minutes then immerse the three uptake capillary tubes in a container of distilled water (at least 200 mL) and leave the pump running for 10 to 20 minutes to flush the system.
3. Remove the capillary tubes from the distilled water. Leave the pump running until the distilled water has been pumped through the system.
4. Switch the VGA-77 off, but leave the inert gas supply on at the regulator. Open the pressure bar and swing the pump tube beds clear of the pump rollers. Remove the pump tubes from the pump rollers and release them from the retaining bracket. Ensure that they are kept completely clear of the rollers while you carry out the next step.
5. Switch the VGA-77 on. This will allow inert gas to flow through the entire system and thus minimize the possibility of residual solutions settling in the lowest section of the tubing. Allow the inert gas to flow for about five minutes.
6. Switch off the VGA-77, and the ICP pump, if necessary.
7. Turn off the inert gas supply at the regulator.

Note Inert gas will flow through the separator even with the VGA-77 switched off.

8. Clean all components as described in section 5.1.
9. Clean your instrument according to its operation manual.

Warning
Be careful when touching the absorption cell or the burner, as they may be very hot. Contact with these components can cause severe burns.
Always ensure that these components are allowed to cool before attempting to remove them from the sample compartment.

3.5 Changing modules

The modular design of the VGA-77 allows easy changing of modules. Follow the steps below.

1. Shut down the system as described in the previous section.
2. Disconnect the sample inlet to gas/liquid separator tubing from the sample inlet, using the reverse of the connection procedure given in section 2.2.11.
3. If you are removing an ICP module, remove the drain tubing from the instrument pump.
4. Disconnect the inert gas connections from the pump unit to the module (refer to section 0, steps 4 and 5).
5. Undo the locking screw on the bottom left of the VGA-77 frame.
6. Ensure the drain tube is completely empty, and remove it from the module.
7. Lift the module up to release the pins at the back of the module from the VGA-77 frame, then remove the module.
8. Immerse the removed module in distilled water, and back flush the lines to clear them of acid remnants. Dry the module in air before using again.
9. Install the required module, following the procedures described in chapter 2.

4. Analytical notes

4.1 Background

The VGA-77 employs continuous flow technology where samples and liquid reagents are pumped together and mixed. The gaseous reactions products are swept by a flow of argon gas into the spectrometer.

Note Nitrogen gas can be used with the AA reagent module.

The following figure shows a schematic diagram of the VGA-77.

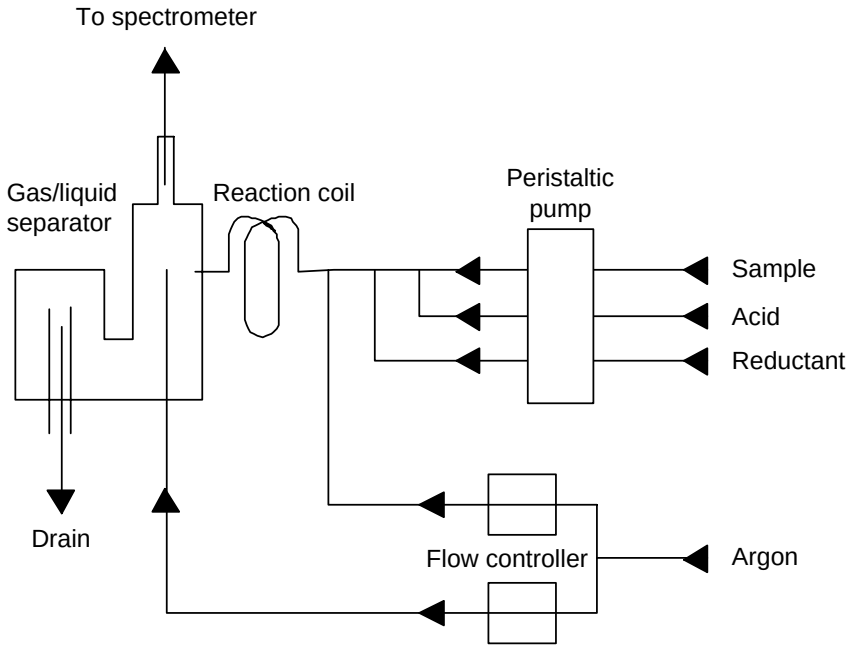

Figure 20. Schematic of the VGA

The peristaltic pump maintains a constant flow of analytical solutions into the accessory.

The sample and acid are allowed to merge first before the reductant, usually sodium borohydride ($NaBH_4$), enters the stream. (For mercury determination, $SnCl_2$ solution is recommended.) Argon is then introduced into the liquid stream and the reaction proceeds while the mixture is flowing through the reaction coil. Vigorous evolution of hydrogen assists the stripping of the hydride (or mercury vapor) from the liquid into the argon.

The gas is then separated from the liquid in the separator. The liquid drains away, or is pumped to waste. At this point a second stream of argon is introduced to ensure that the vapor stream is not saturated with water vapor and does not condense in the sample introduction system.

The vapor containing the element of interest then passes out of the separator into the spectrometer where it is analyzed.

As the VGA-77 produces a continuous signal, you should use the integration mode with Varian AA or ICP-OES systems. (Varian AA users can also use PROMT mode.) ICP-MS users should select the mode 'Peak hopping' with a Dwell time of around 400 µs and 50-100 scans per replicate.

4.2 Factors affecting the formation of hydrides

4.2.1 Acid concentration

The concentration of acid will affect the efficiency of hydride formation in the VGA-77. You must ensure that the acid concentrations of blank, standard and sample solutions are the same.

For multi-element analysis, a compromise acid concentration will be required.

Note The use of oxidizing acids (e.g. H_2SO_4, $HCLO_4$) should be avoided. (See section 4.2.2.)

4.2.2 Oxidation state

The hydride-forming elements may exist in more than one oxidation state in samples and standards. This can have dramatic effects on the measured signal.

For example, for Te and Se, a 10x or more increase in the signal intensity is observed if the lower oxidation state is prepared.

Solutions containing H_2SO_4 and $HClO_4$ acids may give little or no signal for any hydride-forming elements. The use of H_2SO_4 and $HClO_4$ is to be avoided.

Sample AND standard AND blank solutions MUST be prepared by a similar method to obtain the lower oxidation state.

4.2.3 Interferences

The measurement of some elements by VGA can be affected by the presence of other elements or molecules in the sample matrix. These reduce the amount of element detected by the spectrometer by adversely affecting the amount of hydride formed.

A list of observed interferences is given in the following table.

Analyte	Severe to moderate suppression >50%	Moderate to slight suppression 10–50%	Not significant suppression <10%
As	Au, Ge, Ni, Pt, Pd, Rh, Ru	Ag, Bi, Co, Cu, Sb, Se, Sn, Te	Al, B, Ba, Be, Ca, Cd, Cr, Cs, Fe, Ga, Hf, Hg, In, Ir, K, La, Li, Mg, Mn, Mo, Na, Pb, Re, Si, Sr, Ti, Tl, V, W, Y, Zr, Zn, Rb
Bi	Ag, Au, Co, Cu, Ni, Pd, Pt, Rh, Ru, Se, Te	As, Cd, Cr, Fe, Ge, Ir, Mo, Sb, Sn	Al, B, Ba, Be, Ca, Cs, Ga, Hf, Hg, In, K, La, Li, Mg, Mn, Na, Pb, Rb, Re, Si, Sr, Ti, Tl, V, W, Y, Zn, Zr
Ge	As, Au, Cd, Co, Fe, Ni, Pd, Pt, Rh, Ru, Sn, Sb, Se	Bi, Cu, Ir, Te	Al, Ag, B, Ba, Be, Ca, Cr, Cs, Ga, Hf, Hg, In, K, La, Li, Mg, Mn, Mo, Na, Pb, Rb, Re, Si, Sr, Ti, Tl, V, W, Y, Zn, Zr
Sb	Au, Co, Ge, Ni, Pt, Pd, Rh, Ru	Ag, As, As, Cr, Cu, Re, Se, Sn	Al, B, Ba, Bi, Ca, Cd, Cs, Fe, Be, Ga, Hf, Hg, In, Ir, K, La, Li, Mg, Mn, Mo, Na, Pb, Rb, Si, Sr, Te, Ti, Tl, V, W, Y, Zn, Zr
Se	Ag, Cu, Ni, Pd, Pt, Rh, Ru, Sn	Au, As, Cd, Co, Fe, Ge, Pb, Sb, Zn	Al, B, Ba, Be, Bi, Ca, Cr, Cs, Ga, Hf, Hg, In, Ir, K, La, Li, Mg, Mn, Mo, Na, Rb, Re, Si, Sr, Ti, Tl, V, W, Y, Zr (Te)
Te	Ag, Au, Cd, Co, Cu, Fe, Ge, In, Ni, Pb, Pd, Pt, Re, Rh, Ru, Se, Sn	As, Bi, Ir, Mo, Sb, Si, W	Al, B, Ba, Be, Ca, Cr, Cs, Ga, Hf, Hg, K, La, Li, Mg, Mn, Na, Rb, Sr, Ti, V, Y, Zn, Zr

% Loss of analyte signal due to element interferences
See reference #1 in section 4.4.9,

4.2.4 Contamination

When first establishing your analytical method you must always check for contamination before carrying out your program.

Note particularly that traces of potassium iodide (KI) will interfere severely with determinations for bismuth, mercury, selenium and tellurium. You must always ensure that the VGA-77 system is completely free of residual iodide ions (e.g., KI) before attempting to determine these elements.

The most practical way of minimizing contamination problems is to provide a separate module (including the reagent containers and pump tubes) for these elements. Section 5.3 lists spares and part numbers.

Another form of contamination can occur when changing from a high level standard to a low level standard. You must make sure that all tubing in the module is thoroughly rinsed.

4.2.5 Memory effects

Because the VGA-77 uses a chemical reaction to produce the elemental hydrides, some memory effects can be encountered in the reaction products when changing between low and high level standards. Always allow several minutes when moving from a high to a low level standard.

You should also ensure that the standards are prepared at the same concentration as the samples.

Certain types of plastic can cause memory effects for mercury. Keep mercury top standard concentration as low as practicable.

4.2.6 Background absorption (AA only)

In general, background correction is not necessary for vapor generation work. Occasional exceptions may be encountered. For example, when determining low level As in the presence of another hydride forming element.

You should establish whether background absorption is occurring before carrying out your analytical program. This can be done by analyzing a sample with background correction on and then repeating the analysis with it off. (Remember to do an instrument zero before each measurement.)

If a significant difference is found between the two measurements, then perform your analyses with background correction on. If there is none, leave the background correction off.

4.3 Laboratory procedures

4.3.1 General

The vapor generation technique demands a particularly high standard of care in all of the activities which affect the accuracy and precision of the analytical result. Scrupulous cleanliness is essential in all laboratory procedures; standards and samples must be meticulously prepared and carefully handled. Strict precautions must be taken to avoid contamination of apparatus and even though laboratory ware is stored under ideal conditions, it should be thoroughly re-washed before use.

Strict care should also be taken to avoid contamination of all reagents and distilled water. Ideally, reagents should be entirely free of the element of interest, but this is obviously impossible for all analyte elements in all reagents. Consequently, you must always establish the level of the analytical signal attributable to analyte in the reagents. It is, of course, standard practice to check the analytical signal from the blank solution before calibrating the instrument and carrying out the analytical program.

Dispose of waste in accordance with relevant safety practices.

4.3.2 Standards

Prepare your calibration standards from stock solutions.

For some samples it will be necessary to compare the calibration slopes using the normal calibration method with those obtained using the standard additions method. If the slope is not the same, you should use the standard additions technique for the analysis.

4.3.3 Reductant—sodium borohydride

The recommended sodium borohydride ($NaBH_4$) concentration is 0.6% w/v. However better results will be obtained for difficult samples containing high concentrations of metals if the sodium borohydride concentration is reduced to 0.3% w/v.

Note Stannous chloride reductant is recommended for mercury determinations. Refer to section 4.4.4.

Always stabilize the solution by first adding sodium hydroxide (NaOH—0.5% w/v). Since sodium borohydride will decompose significantly in one or two days, you should not prepare more than 500 mL at a time. At a flow rate of about 1 mL per minute, this should be enough for continuous operation over a typical working day. Stability may be improved by passing the solution through a 5 micron filter. You can also extend the working life of the solution by storing at 5 °C. (The solution should remain stable for approximately one week if stored at 5 °C.) Allow the solution to reach room temperature prior to analysis.

4.3.4 Pump tubing

The pump tubing should be checked regularly by checking the flow-rate (refer to section 3.1.2 'Pump adjustment').

Note When concentrated acid is first pumped through the acid tube, the inside of the tubing may turn white, but this does not impair the efficiency of the tube.

Ensure samples, reagents and standards are at room temperature prior to analysis. The VGA-77 pump will not operate correctly with hot or cold solutions as the pumping rate may vary with solution temperature.

4.3.5 Sources (AA only)

Hollow cathode lamps or UltrAA lamps can be used for all VGA-77 methods for AA analysis.

4.4 Basic methods

The hydride-forming elements may exist in more than one oxidation state in samples and standards. (Refer also to section 4.2.2.) The following analytical methods for sample and standard have been developed to ensure samples and standards are present in the correct oxidation state.

4.4.1 Antimony

Prepare samples in at least 1 M hydrochloric acid and ensure that any analyte present as Sb^{V} is reduced to Sb^{III} by the action of potassium iodide at a concentration of 1% w/v. Reduction is spontaneous and heating should not be required.

Reductant container:	$NaBH_4$ 0.6%, NaOH 0.5%
Acid container:	5 to 10 M HCl

4.4.2 Arsenic

Note If arsenic and selenium are both to be determined from the same sample, determine selenium first, and avoid KI in samples or standards. You can then determine arsenic after the KI reduction step and any other appropriate treatment (such as the addition of urea if excess nitric acid is present).

Arsenic in the sample must be in the inorganic form, otherwise digestion will be necessary.

If digestion is necessary, use acid digestion, ensuring no residual oxidizing acid is present (see section 3.2.2), or ashing with an appropriate ashing aid. Simple dry ashing is not recommended.

Prepare samples in at least 1 M hydrochloric acid.

Ensure that any analyte present as As^{V} is reduced to As^{III} by the action of potassium iodide at a concentration of 1% w/v.

Reduction will take about 50 minutes at room temperature. The reduction can also be carried out at 70 °C in about four minutes; however you must cool the samples and standards to room temperature prior to analysis. Since the pumping rate may vary with solution temperature, the VGA-77 pump will not operate correctly with hot solutions.

If the reduction step is omitted, and the analyte is retained as As^{V}, the analytical sensitivity is about 20-30% of that obtained for As^{III}. If the original solution contains As^{III}, reduction by potassium iodide is not required.

Reductant container:	$NaBH_4$ 0.6% (see also above) NaOH 0.5%
Acid container:	5 to 10 M HCl

4.4.3 Bismuth

The presence of potassium iodide will severely suppress the analytical response. Always ensure that the VGA-77 system is completely free of potassium iodide before performing bismuth determinations.

Note To avoid contamination, it is recommended that you dedicate a separate module to the analysis of those elements requiring pre- reduction with KI—As, Sb.

Prepare samples in 1 M hydrochloric acid.

Reductant container:	$NaBH_4$ 0.6% NaOH 0.5%
Acid container:	5 M HCl (Higher acid concentrations will depress the analytical signal.)

4.4.4 Mercury

Traces of potassium iodide will interfere severely with the production of mercury vapor and the analytical response may be completely suppressed. Always ensure that the VGA-77 system is completely free of potassium iodide before performing mercury determinations.

Note To avoid contamination, it is recommended that you dedicate a separate module to the analysis of those elements requiring pre-reduction with KI—As, Sb.

The mercury in the sample must be in the inorganic form, otherwise digestion or use of releasing agents (e.g. $CdCl_2$), will be necessary.

If digestion is necessary, use acid digestion, or ashing with an appropriate ashing aid. Simple dry ashing is not recommended as the mercury will be lost.

Dilute mercury solutions tend to be unstable; all analytical solutions should be stabilized by the addition of nitric acid (5% v/v) and hydrochloric acid (5% v/v). Prepare fresh standards daily.

If you are using the AA module:

Acceptable results can be obtained with the standard absorption cell, however the flow-through mercury cell is recommended since this will generally provide better analytical sensitivity and precision.

Remember that AA mercury determination is a cold vapor technique. Mercury is best determined with a cold cell as the analytical sensitivity is reduced when the cell is heated. Under no circumstances should the flow-through cell be heated.

Caution — Heating the flow-through cell may damage it

If you are experiencing problems with carry over of water vapor into the cell (or condensation in the cell), heating of the flow cell can eliminate this. One approach to heating the cell is to use the ETC-60 Electrothermal Temperature Controller programmed at 300°C. Alternately, another switch in heat source (like a lamp) can reduce the occurrence of this problem.

For locations where the discharge of mercury vapor in nanogram quantities is not permitted, the standard absorption cell is not suitable and you should use the flow-through mercury cell together with a suitable trap. Refer to section 0.

Mercury should be determined using stannous chloride as the reductant.

Reductant container:	$SnCl_2$ (25% w/v) in HCl (20% v/v)
Acid container:	H_2O

Note — To prepare the $SnCl_2$ solution, add $SnCl_2$ crystals to concentrated HCl and warm the mixture on a hot plate to complete dissolution before adding the water. A piece of granulated tin added to the mixture will reduce any Sn(IV) to Sn(II) and produce a clear solution.

Note — Mercury suffers from memory effects as it adheres to plastic. Keep concentrations low to minimize these memory effects.

An alternative method for mercury determination with AA uses the $NaBH_4$ reduction procedure. In this method, it is preferable to use a lower concentration of sodium borohydride than would normally be used for the hydride-forming elements. The concentration of acid pumped through the VGA-77 system is generally not critical.

For ICP analysis (OES/MS), ensure the spray chamber drain is clamped to avoid loss of the mercury analyte.

Reductant container:	$NaBH_4$ 0.3%, NaOH 0.5%
Acid container:	5 M HCl

A lower analytical signal may be obtained with this method than with the stannous chloride method.

4.4.5 Selenium

Note See also section 4.4.8 ‘Additional notes’ at the end of this section.

The selenium in the sample must be in the inorganic form, otherwise digestion will be necessary.

If digestion is necessary, use acid digestion, or ashing with an appropriate ashing aid. Simple dry ashing is not recommended because selenium is highly volatile and recovery will be poor.

Se^{VI} is not quantitatively recovered by hydride generation and must be reduced to Se^{IV} by warming with concentrated hydrochloric acid. Prepare the samples in 6-7 M hydrochloric acid (use of a lower acid concentration will result in greater inter-element interferences), heat at 70-90 °C for at least 10 minutes. Cool to room temperature before analysis.

Reductant container:	$NaBH_4$ 0.6% NaOH 0.5%
Acid container:	10 M HCl

4.4.6 Tellurium

The presence of potassium iodide will severely suppress the analytical response. Always ensure that the VGA-77 system is completely free of potassium iodide before performing tellurium determinations.

Note To avoid contamination, it is recommended that you dedicate a separate module to the analysis of those elements requiring pre-reduction with KI (i.e. As or Sb).

Te^{VI} is not quantitatively recovered by hydride generation and must be reduced to Te^{IV}. Prepare the samples in 6-7 M hydrochloric acid, heat at 70-90 °C for at least 10 minutes and cool to room temperature before analysis.

Reductant container:	$NaBH_4$ 0.6% NaOH 0.5%
Acid container:	5 M HCl (Higher acid concentrations will reduce the analytical signal.)

4.4.7 Tin

The best results for tin will generally be obtained from solutions prepared in 1% tartaric acid. Also, a study[2] has shown that the addition of L-cysteine greatly improves tin determination by hydride generation. The L-cysteine reduces metal interferences and improves precision and sensitivity. Some improvement in calibration linearity has also been noted.

The concentration of acid pumped into the VGA-77 is also critical in tin determinations, and the analytical signal will be severely depressed at concentrations higher than 0.5 M. (Refer to section 4.2.1 'Acid concentration'.)

When determining tin using the AA technique, it is essential to determine tin at the 286.3 nm wavelength and 0.2 nm slit since this will provide the best combination of analytical sensitivity and dynamic range. The 235.5 nm line commonly used for flame and furnace AA gives very poor sensitivity and the 224.6 nm line shows very little increase in analytical response above approximately 0.3 absorbance.

Reductant container:	$NaBH_4$ 0.6% NaOH 0.5%
Acid container:	0.5 M HCl
Sample	1% Tartaric acid controlled pH (2.0 to 3.0)
Alternative method[2]	
Reductant container:	$NaBH_4$ 0.5% NaOH 0.1%
Acid container:	D.I. H_2O
Sample	1% Tartaric acid 1% L-cysteine

4.4.8 Additional notes

1. If arsenic and selenium are both to be determined from the same sample, determine selenium first and avoid KI in samples or standards. You can then determine arsenic after the KI reduction step and any other appropriate treatment (such as the addition of urea if excess nitric acid is present).

2. For the determination of arsenic and selenium in many practical samples containing high concentrations of metals such as copper, iron or nickel, fewer interferences have been observed using 0.3% w/v $NaBH_4$ solution concentration (rather than 0.6% w/v). Use of the lower reductant concentration may, however, be less sensitive.

3. You can minimize interferences of transition metals such as cobalt, copper, iron, and nickel on arsenic and selenium by preparing samples in 6-7 M HCl. With lower acid concentrations, greater inter-element interferences are present.

4. Co-precipitation methods using lanthanum compounds have also been found to be useful.

4.4.9 References

1. Smith, A.E., 'Interferences in the determination of elements that form volatile hydrides with $NaBH_4$ using AAS and Ar/H_2 flame.', *Analyst*, May, 1975, 100, 300-306

2. Varian AA-at-Work, 1992, October, No. 107

4.4.10 Additional references

The following references are recommended:

Varian Instruments At Work
Numbers AA - 38, 44, 50, 51, 56, 60, 65, 78, 82, 86, 87, 105, 107

Spectroscopy, 1985, Vol 1 (0), 60

Appl. Spectrosc., 1985, Vol 39 (1), 48

Jiri Dedina and Dimiter L. Tsalev, Hydride Generation Atomic Absorption Spectrometry. Published by John Wiley and Sons, Edited by J.D. Winefordner. ISDN 0 471 953644

5. Maintenance and spare parts

5.1 Cleaning procedures

5.1.1 General

The VGA-77 uses high concentrations of HCl. Continual exposure to HCl fumes may damage the instrumentation. Maintain an efficient exhaust system during VGA determinations and remove HCl solutions from the VGA-77 and the spectrometer when you finish your analyses.

Always clean up any spilt liquids immediately. The front of the spectrometer, the burner/torch compartment and the VGA-77 should be cleaned daily with a soft cloth. If necessary, use a cloth dampened with distilled water.

Observe the shut down procedure as described in section 3.4.

5.1.2 Absorption cell

This section applies to AA modules only.

Always clean the absorption cell thoroughly immediately after use, when contamination is suspected while conditioning the system, or whenever the system has been left unused for some time. Throughout the cleaning procedure remember that the cell is fragile and must be handled with appropriate care.

Warning
Before touching the cell remember that it may be very hot and could cause serious burns.
Always turn the flame off and allow the cell to cool before attempting to remove it from the sample compartment.

1. Disconnect the black fuoro-elastomer tubing from the cell inlet.
2. Release the spring clips and remove the absorption cell from the cell support.
3. Soak the absorption cell in dilute nitric acid for at least 30 minutes.
4. Rinse thoroughly with distilled water and allow it to air dry in a dust-free location.
5. If the cell has been exposed to contamination with potassium iodide, soak the cell in sodium hydroxide solution (0.5% w/v) for at least 30 minutes. Wash thoroughly with dilute hydrochloric acid and then wash thoroughly with distilled water. Allow to air dry in a dust-free location.

Caution

Do not leave the cell in the sodium hydroxide for too long because this solution may accelerate cell devitrification.
Avoid handling the central part of the quartz cell with bare hands after it has been cleaned or while it is in use.

The working life of the cell will depend on the type of analytical programs carried out. At some stage, the quartz will start to turn white indicating the onset of devitrification. Initially, devitrification will not degrade the analytical performance, but eventually the devitrified area will extend over most of the cell at which point it may be necessary to discard the cell.

If devitrification is excessive, the cell will eventually crack spontaneously or fail through thermal shock.

Whether the cell becomes devitrified or not, and even with meticulous cleaning, the inside surface may deteriorate to the extent that the analytical signal will be suppressed. You should regularly monitor the performance of the cell using absorbance measurements obtained from standard solutions. Discard the cell as soon as the results of this monitoring become unacceptable.

Note

When a significant number of samples are being analyzed, the use of a drierite trap inserted between the absorption cell and the output of the gas/liquid separator will protect the absorption cell and extend its lifetime. (Refer to Varian AA-at-Work, 1986, October, No. 65.)

Under some circumstances, the centre section of the cell may gradually soften in the flame and sag. If uncorrected, this may become so severe that alignment of the cell within the optical path is impossible. When sagging is first noticed, it can be corrected by simply turning the cell over so that it will return to its normal shape the next time it is heated.

5.1.3 Gas/liquid separator

As with the cell, the gas/liquid separator must be cleaned immediately if contamination is suspected during conditioning, or whenever the system has been left unused for some time. Do not allow hydrochloric acid solutions to remain in the separator.

Warning
Contact with concentrated acids can cause severe burns.
Always wear protective clothing and gloves while cleaning the separator.

1. Disconnect the tubing from the vapor outlet of the separator.
2. Disconnect the tubing from the sample inlet of the separator.
3. Carefully remove the rubber mounting strap holding the separator in place.
4. Disconnect the drain tubing from the drain in the bottom of the module. You may now lift the separator out of the module.
5. Disconnect the tubing from the inert gas inlet of the separator.
6. If the separator has been exposed to solutions containing potassium iodide, soak the separator in sodium hydroxide solution (0.5% w/v) for at least 30 minutes. Wash thoroughly with dilute hydrochloric acid and then wash thoroughly with distilled water. Allow to air dry in a dust-free location.

Note To avoid KI contamination, it is recommended that you dedicate a separate module to the analysis of those elements requiring pre-reduction with KI (i.e. As or Sb).

7. If the separator has not been exposed to potassium iodide solutions, it may be treated in the same way as the absorption cell.
8. Refit the separator into its mounting bracket, secure it with the retaining strap and reconnect all tubing. If the system is not to be used for some time, the separator should be filled with distilled water.

5.1.4 Tubing

Pump tubes

When the system is not being used, the pressure bar should be released, the pump tubes removed from around the rollers and released from the retaining bracket. This will minimize distortion of the tubes and help to prolong their working life.

To reduce mechanical wear of the pump tubes, the outside of the tubes and the surface of the pump rollers should be sprayed daily with a silicone lubricant.

If the procedure specified in section 3.4 is followed, the system tubing will generally remain clean, however the efficiency of all pump tubes will eventually be degraded to the point at which they must be replaced. You should regularly monitor the performance of each pump tube using flow rate measurements (see section 3.1.2.). Discard the pump tubes as soon as the results of this monitoring become unacceptable.

Note The tubes connecting the black-black pump tubes to the pump module may occasionally need to be replaced. To do this, cut four 2 cm lengths of the thinner black Viton tubing supplied. Place these over each end of two of the black-black pump tubes.

Fluoro-elastomer tubing

The fluoro-elastomer tubing connecting the gas/liquid separator to the absorption cell is particularly susceptible to contamination with potassium iodide. To avoid this, it is recommended that you dedicate a separate module to the analysis of those elements requiring pre-reduction with KI (i.e. As or Sb).

The cleaning procedure for the fluoro-elastomer tubing is as follows:

If there is no KI contamination, you can clean the tubing by flushing it well with distilled water.

If there is KI contamination, you need to remove traces of KI as follows:

1. Disconnect and remove the tubing.
2. Soak the tubes in sodium hydroxide solution (0.5% w/v). Wash thoroughly with dilute hydrochloric acid and then wash thoroughly with distilled water.
3. Allow the tubes to air dry in a dust-free location.
4. Reconnect the tubing.

An alternative method of removing traces of iodine from the tubing and gas liquid separator is to pump a freshly prepared 1% sodium thiosulfate solution through the system for 5-10 minutes. You must then remove the thiosulfate by pumping distilled water through the system for 5-10 minutes.

5.2 Replacement procedures

5.2.1 Pump tubes

To remove the pump tubes, use the reverse procedure of that given in section 2.2.8.

5.2.2 Reaction coil

1. Remove the gas/liquid separator as described above.
2. Remove the thumbscrew holding the reagent manifold cover in place. Remove the cover by pulling the top of the cover away from the manifold block and pushing the cover down.
3. Remove the black fluoro-elastomer sleeve from the end of the reaction coil. Pull the end of the reaction coil through the hole in the manifold block, then pull the reaction coil out of the channel.
4. Slide the 'T' connection and the pump tubing connector out of their slots. You will find it easier if you remove all of the 'T' pieces and pump connectors.
5. Hold the upper 'T' piece and sleeve firmly with one hand and pull the reaction coil out of the sleeve.
6. Fit the new reaction coil into the sleeve, then replace all of the pump tube connections and 'T' connections into their slots.
7. Wind the reaction coil around the channels and out through the hole in the manifold block. Ensure that there are no kinks in the tubing.
8. Fit the black fluoro-elastomer sleeve onto the end of the reaction coil.
9. Replace the manifold cover.
10. Replace the separator.

5.2.3 Uptake capillary tubes

To replace a capillary tube:

1. Remove the separator and manifold cover as described above.
2. Slide the pump tubing connector out of its slot.
3. Pull the capillary out of its sleeve.
4. Push the end of the new capillary into its sleeve.
5. Replace the connector into its slot.
6. Replace the cover.

5.2.4 Fuses

Fuses have a code marked on the cap (e.g., T 2A H250V). This refers to the fuse characteristic ('T' - time lag, 'F' - fast acting), the current rating ('x' amperes), the breaking capacity ('H' - heavy, 'L' - low), and the voltage rating ('y' volts).

Warning
To prevent reduced safety protection or unwanted fusing, always ensure that the marking on the fuse matches the screening shown adjacent to the voltage selector switches.

Check the fuses as follows:

1. Disconnect the unit from the mains power supply.
2. Undo the fuse cap by pressing the cap and turning it counter-clockwise.
3. Pull the cap out carefully. The fuse should be held in the fuseholder in the fuse cap.
4. Check that the fuse is the correct type and that it is not damaged. If necessary, replace the fuse in the holder.
5. Place the fuse into the cap, push the cap in, and turn the cap clockwise.
6. Reconnect the unit to the mains power supply.

5.3 Spare parts

Note Use only Varian supplied parts unless otherwise indicated.

The following spare parts are available from Varian for your VGA-77:

Module for AA includes reagent module, tubing and connectors	99 100621 00
Module for ICP includes module, tubing and connectors	99 100622 00
Absorption cell for AA 2 cells, separator to cell tubing (fluoro-elastomer)	99 100400 00
Flow through mercury cell kit cell, separator to cell tubing (fluoro-elastomer)	99 100407 00
Cell holder for Mark 7 burner	01 106549 90
Cell holder mounting kit for Mark VI burner	01 103759 90
Cell holder for Mark V burner mount	01 103177 90
Cell holder mounting kit for Mark V burner	04 101173 00
Tubing kit for AA	99 100619 00
Tubing kit for ICP	99 100618 00
Gas/liquid separator kit for AA separator and rubber mounting strap	99 100711 00
Gas/liquid separator kit for ICP separator, tubing and rubber mounting strap	99 100569 00
Fuse, T0.2AH0250V IEC sheet 5, 5 x 20 mm	19 100093 00
Pump tubes, black/black (pack of 12)	37 100272 00
Pump tubes, purple/black (pack of 12)	37 100273 00
Polyethylene capillary tubing (1 metre lengths)	24 100205 00
Fluoro-elastomer tubing, small (1 metre lengths)	37 100268 00
Fluoro-elastomer tubing, AA (0.66 metre lengths)	37 100263 90

(ID = 0.110 inch)	
Drain tubing (10 mm)from gas-liquid separator (2 metre length)	37 100092 00
Reagent vessel, 500 mL	66 100116 00
Replacement drip tray	70 100172 00

6. Appendix–AA Performance log

Date	Operator	Uptake rate	Element	Concentration	Abs

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