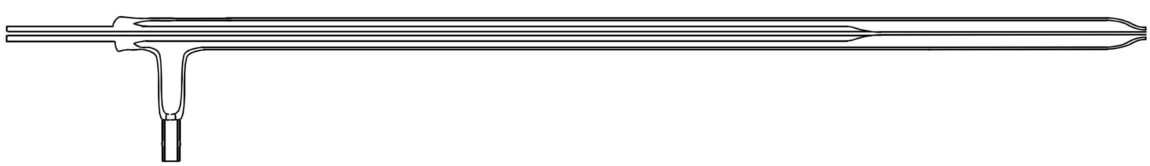
MEINHARD®

INSTRUCTION MANUAL FOR THE DIRECT INJECTION HIGH EFFICIENCY NEBULIZER



Meinhard Glass Products

Meinhard Glass Products
700 Corporate Circle, Suite A, Golden, CO 80401 USA
Tel: 303.277.9776 Fax: 303.216.2649 Email: Sales@meinhard.com
Web: www.meinhard.com

CONTENTS **PAGE**

INSTRUCTIONS FOR EXPERIENCED DIHEN USERS

The first-time user should refer to INSTRUCTIONS FOR INSTALLING AND OPERATING THE DIHEN on page 4 for a more detailed explanation of these following steps. The summary instructions listed below are intended for regular users.

Step #1- *Configure the ICP instrument*. Remove the injector tube from the ICP torch and insert the DIHEN adapter into the plasma torch. Configure the ICP system for operation with the demountable torch.

Step #2 - *Start the plasma with the DIHEN shell* (only if a new ICP system is used, or for testing purposes, as necessary).

Step #3 - *Connect the DIHEN solution uptake line*.

Step #4 - *Connect the DIHEN gas supply line*.

Step #5 - *Insert the DIHEN into the ICP torch*.

Step #6 - *Ignite the plasma.* Ignite the plasma at 1200 W with an injector gas flow rate of 0.25 L/min.

INTRODUCTION AND BACKGROUND

The direct injection high efficiency nebulizer (DIHEN) was introduced as a commercial micronebulizer by J.E. Meinhard Associates, Inc., in March 1998.[i-iii] The DIHEN was developed based on two conclusions from previous studies on the high efficiency nebulizer (HEN):[iv,v] at solution uptake rates of less than 100 L/min, the HEN-spray chamber combination offers detection limits that are similar to those of conventional pneumatic nebulizers operated at 1 to 2 mL/min,[v] and (2) the primary aerosol produced by the HEN[iv] exhibits droplet size distributions that are smaller and narrower than those reported for the direct injection nebulizer (DIN).[vi]

A number of unique benefits can be realized through direct nebulization into the plasma. These advantages include, 100% analyte transport efficiency, improved precision, low solution flow rates (1 to 100 L/min), no loss of volatile analytes, and low nebulizer gas consumption (less than 0.5 L/min). The DIHEN combines the simplicity and low cost of the Meinhard® nebulizer with the advantages of direct introduction of aerosol to the plasma.

A schematic diagram of the DIHEN is shown in Figure 1. The dimensions for the nebulizer tip of the DIHEN are similar to those of the high efficiency nebulizer (HEN),[iv] however, the DIHEN is 3 to 4 times longer than conventional HENs.

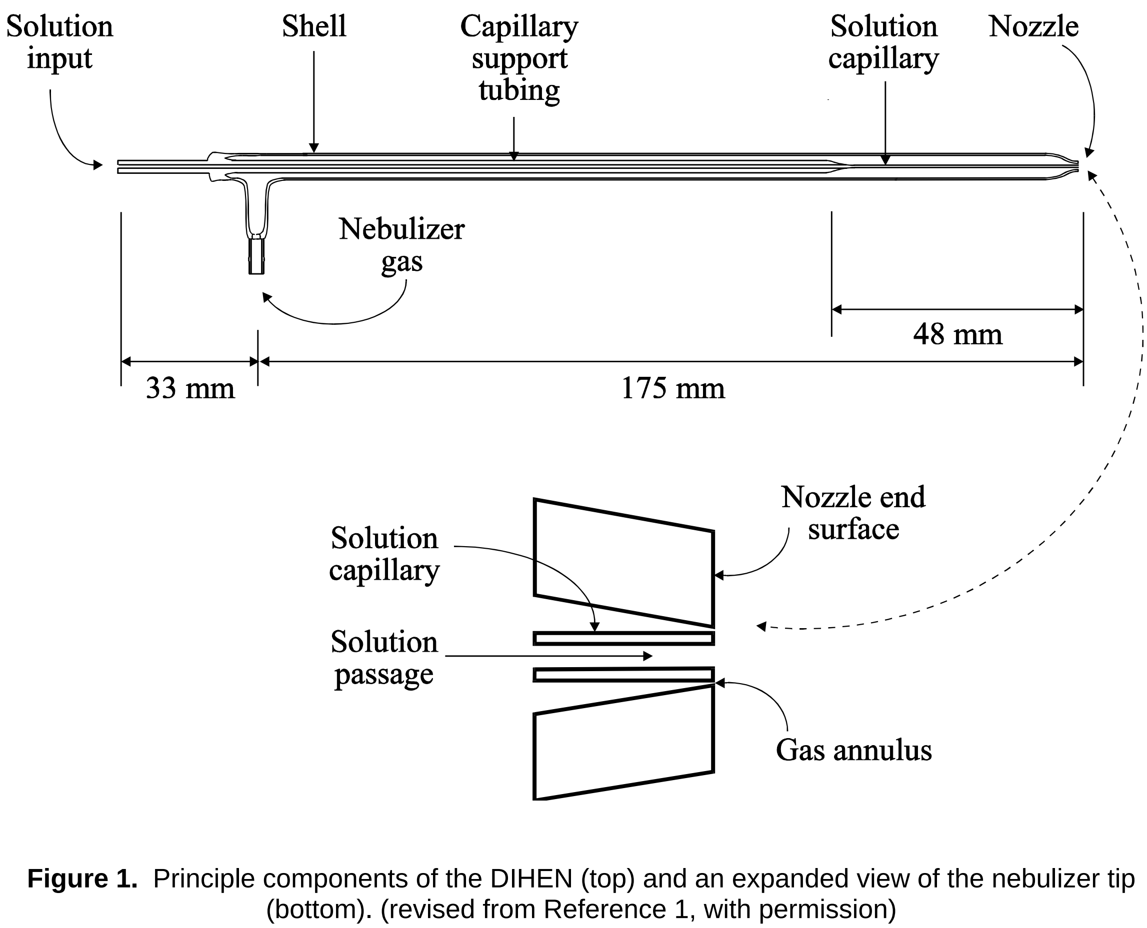


Figure 1. Principle components of the DIHEN (top) and an expanded view of the nebulizer tip (bottom). (revised from Reference 1, with permission)

The DIHEN is well suited for the analysis samples that are limited, expensive, hazardous, or volatile. In using the DIHEN, the analyst should keep two points in mind. First, the solution capillary in the DIHEN tapers from the back-end of the nebulizer to the nozzle tip. Similar to other concentric nebulizers, the solutions should be clean of particulate matter otherwise capillary blockage may result. If the solution capillary or gas annulus is clogged, please refer to the Appendix ("Maintenance tips for users of the Meinhard® DIHEN") to this manual. Second, the DIHEN is more delicate than conventional concentric nebulizers because it is 3 to 4 times longer than its shorter counterparts. The DIHEN is rather robust, but the nozzle and/or the capillary will not survive being dropped or excessively torqued. Extreme care and common sense are essential when setting up the DIHEN for elemental analysis.

OPERATING THE DIHEN WITH PLASMA SOURCE SPECTOMETRIES

In principle, the DIHEN can be easily interfaced with any type of plasma source spectrometer, in particular with inductively coupled plasma atomic emission spectroscopy and mass spectrometry (ICPAES and ICPMS, respectively). A demountable torch assembly is necessary when using the DIHEN. The injector gas tube is replaced with the DIHEN, which is mounted in a DIHEN adapter. The DIHEN adapter supports the DIHEN in the center of the ICP torch just at the base of the plasma. Figure 2 shows the principle components for interfacing the DIHEN with the demountable torch of an Elan 6000 ICPMS (Perkin-Elmer/Sciex Corporation, Norwalk, CT, USA) instrument. Adapters are available for other brands of ICP instrumentation.

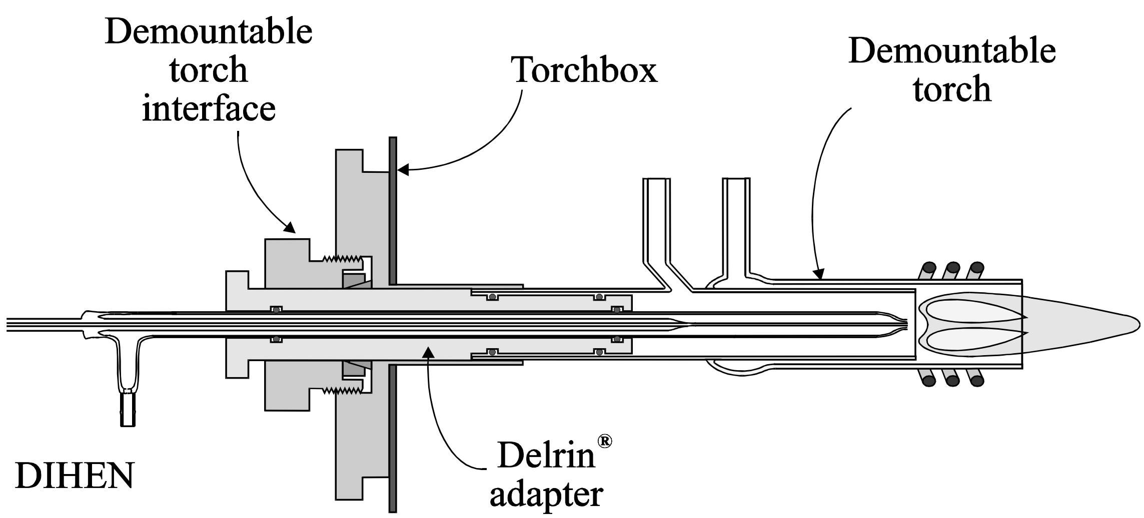


Figure 2. Schematic diagram depicting the DIHEN interfaced with the Elan 6000 demountable torch interface. (revised from Reference 1, with permission)

INSTRUCTIONS FOR INSTALLING AND OPERATING THE DIHEN

Meinhard Glass Products includes a dummy nozzle with each DIHEN to use for familiarization purposes. Meinhard Glass Products strongly recommends that inexperienced users practice with the dummy nozzle before igniting the plasma with the DIHEN in position. This DIHEN shell has a small opening (0.010" to 0.015") and will present a back pressure of 3 to 15 psi when the carrier flow is set in the range of 0.5 to 1.0 L/min.

Step #1 *- Initial inspection*. Upon receiving your Meinhard DIHEN, carefully remove it from the plastic packaging and inspect it for any damage during shipping. The DIHEN is most susceptible to damage or breakage at the nebulizer tip, and the inside and outside positions where the solution uptake arm joins to the nebulizer shell.

Step #2 *- Configuring the ICP instrument*. Insert the DIHEN adapter into the demountable plasma torch of the ICP instrument. A small amount of distilled-deionized water (DDW) may be applied on the o-rings before insertion to reduce the friction between the o-rings and the torch. **Caution**: please don't place any lubricant (e.g. grease, lubriseal, teflon lubricant, etc.) other than DDW on the o-rings as this will compromise the o-rings effectiveness. The demountable plasma torch and adapter should then be firmly fixed inside the torchbox of the ICP instrument, before the DIHEN is inserted. (In some instruments, the DIHEN must be inserted at this stage, please proceed to step #5, then steps #3 and 4).

Step #3 *- Connecting the DIHEN solution uptake line*. It is recommended that the solution input to the DIHEN be connected using the Meinhard "SB Fittings Assembly (Kit #1-Micro)" or the Meinhard "SB Fittings Assembly (Kit #1)." The "SB Fittings Assembly (Kit #1-Micro)" can be used to reduce the dead volume of the DIHEN for microscale flow injection analysis (FIA) or for microbore high performance liquid chromatography (HPLC) applications. The proper use of these assemblies is described below under the section entitled DEAD VOLUME REDUCTION IN THE DIHEN. Connect the solution delivery line to the DIHEN solution uptake arm. For the best precision and analytical results, we recommend pulseless solution delivery methods such as a syringe or gas displacement pump. A peristaltic pump may be used with narrow bore peristaltic tubing, but precision may be compromised.

Step #4 *- Connecting the DIHEN gas supply*. On a clear workbench, prepare the DIHEN for connection to the nebulizer gas supply. Using the Meinhard "High Pressure Fitting Assembly (Fit Kit #2)," place the small Swagelok nut over the gas side arm of the nebulizer. Next, carefully slide the o-ring over the maria (the small bump on the gas supply arm). Place the front ferrule over the maria and screw the Swagelok nut to the union body. The DIHEN is now ready for connection to the gas supply via a mass flow regulator on the instrument. Alternatively, an independent gas flow line may be used with a separate mass flow regulator. **Caution**: Please do not overtighten the nut to the union body or the DIHEN may be broken! Just tighten the nut until it is snug, and no gas leaking occurs.

Step #5 *- Inserting the DIHEN into the ICP torch*. After the gas and solution lines are firmly attached to the DIHEN, gently insert the DIHEN into the ICP torch. If the inner adapter o-rings prevent easy insertion of the DIHEN into the plasma torch, place a small amount of distilled-deionized water (DDW) on the DIHEN before insertion to reduce the friction between the o-rings and the nebulizer body. **Caution**: Please do not place any lubricant (e.g. grease, Lubriseal, Teflon lubricant, etc.) other than DDW on the DIHEN as this will compromise the o-ring's effectiveness, and may introduce contamination in analytical measurements. **Caution**: Insert the nebulizer tip straight through the adapter. If the nebulizer tip is pressed against the wall of the adapter, the nebulizer tip can be chipped or broken. The tip of the DIHEN should be positioned approximately 2 mm below the outlet of the intermediate plasma tube. It advisable to start lower, and to practice with the dummy nozzle.

Step #6 - *Igniting the plasma*. The DIHEN has been used for hundreds of hours on some instruments without any difficulty in igniting the plasma or damage to the nebulizer tip. However, “first-time users” should use a DIHEN shell (without the solution capillary inserted) to test the interface and ignition process. **This approach is recommended for all first-time users for practice on plasma ignition.** When possible, ignite with an injector gas flow rate of 0.25 L/min, but without nebulization. Approximately 1200 W may be applied to ignite the plasma. Depending on the instrumental configuration, it may be possible to retract the DIHEN during ignition and then slide it to the analytical position after the plasma has lit. **Caution:** If moving the DIHEN while a plasma is lit, extreme caution should be exercised so as not to insert the tip of the DIHEN into the plasma. This will result in unrecoverable damage due to melting of the nebulizer tip.

OPERATIONAL CHARACTERISTICS OF THE DIHEN

The reader is referred to Reference 1 for details on the operating characteristics of the DIHEN with ICPMS. For comprehensive reviews of sample introduction into plasmas and fundamentals on aerosol generation and transport, please refer to References ii,vii-xii. The primary differences of the operating characteristics of the DIHEN, as opposed to conventional concentric nebulizers, are presented here.

Nebulizer gas flow rate. For ICPMS, the DIHEN optimally operates at very low nebulizer gas flow rates (for instance ~0.25 L/min for the Elan 6000, but should be optimized by the user). This is in sharp contrast to conventional nebulizers which optimally operate at 0.8 to 1 L/min. Sensitivity goes up as the nebulizer gas flow rate is reduced (Figure 3). This is likely the result of lower mean droplet velocities and narrower droplet velocity distributions which serve to increase the residence time of analyte droplets in the plasma.[i] However, there is a minimum nebulizer gas flow rate which should be used. If the nebulizer gas flow rate is too low, an annular channel is not formed and the nebulizer may begin to “sputter” generating very large droplets. When this condition is reached, the plasma may become unstable and extinguish. Further, the very large droplets will contribute extensively to the metal oxide to metal ion ratios in ICPMS.

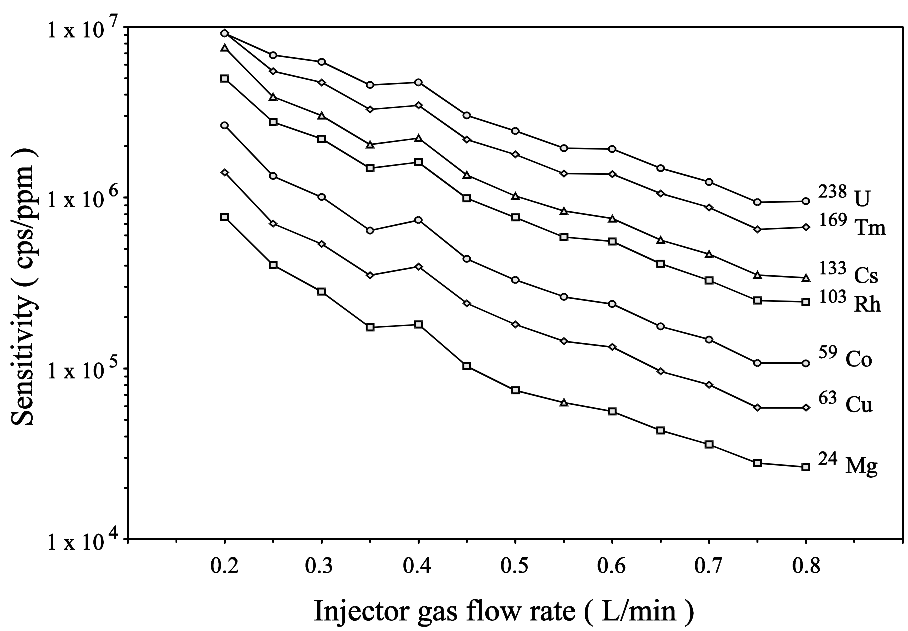


Figure 3. Sensitivity as a function of injector gas flow rate for the DIHEN operated at a solution uptake rate of 11 L/min and an rf power of 1500 W using an Elan 6000 ICPMS. (from Reference 1, with permission).

ICP forward power. The optimal plasma forward power is higher (~ 1500 W) than that for conventional sample introduction devices (1100 - 1300 W). This is due to the cooling effect of the *primary* aerosol. The higher power plasma can more effectively desolvate-vaporize-atomize-ionize the sample droplets in the plasma. This results in enhanced sensitivity. Depending on the particular application, the analyst should determine the optimal plasma power.

Solution flow rates. The DIHEN is operated at solution flow rates of 1 to 100   L/min, although it should be possible to operate the DIHEN at even lower solution flow rates. Depending on the particular application, the analyst should determine optimal solution flow rates. Ideally, one should use a pulseless form of sample delivery for these low solution flow rates, that is, a syringe pump or gas displacement pump, but these flow rates can be achieved using narrow-bore peristaltic tubing.

Analyte transport efficiency. The DIHEN introduces 100% of the sample solution into the plasma. This is in sharp contrast to conventional nebulizer-spray chamber combinations where up to 99% of the analyte is directed to the drain of the spray chamber.[vii,viii]

DEAD VOLUME REDUCTION IN THE DIHEN

The current dead volume of the DIHEN is on the order of 50 to 60   L. A reduction in the dead volume is crucial for applications involving μFIA, μHPLC, or capillary zone electrophoresis. A reduction in the dead volume will reduce band broadening due to analyte dispersion, improve wash-in/out characteristics, reduce memory effects, and further reduce sample consumption.

It is easy to reduce the dead volume to < 2 μL when desired. To reduce the dead volume, a capillary tubing (0.016 in. o.d.) is inserted into the back of the DIHEN to the point where the capillary tapers. Representative dead volumes for pieces of tubing 250 mm in length are given in Table 1. Tubing can be obtained either from Meinhard Glass Products or from Cole-Parmer (Vernon Hills, IL, USA).

Table 1. Dead volume reduction in the DIHEN

Capillary tubing i.d. μm (in.)	Capillary tubing o.d. (in.)	Dead volume* μL
51(0.002)	(0.014)	< 2
102 (0.004)	(0.016)	< 2.5
152 (0.006)	(0.016)	< 5
203 (0.008)	(0.016)	< 8.5

* Values for dead volume presented here are slightly higher than calculated to be conservative. Other sources of dead volume result from the injection valve and the connections.

To connect the capillary tubing to the DIHEN, one should obtain an SB Fittings Assembly (Fit Kit #1-Micro) from Meinhard Glass Products. To install the kit, simply follow these steps with reference to Figure 4. Please note that more efficient schemes can be used than those outlined here. However, the below steps will reduce the risk of damaging the DIHEN by reducing strain placed on the device during the kit installation.

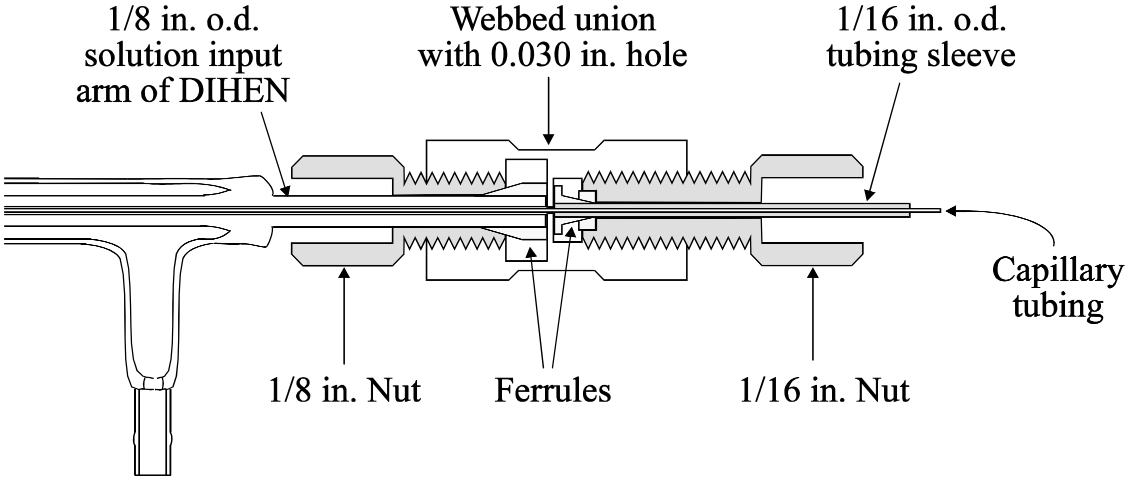
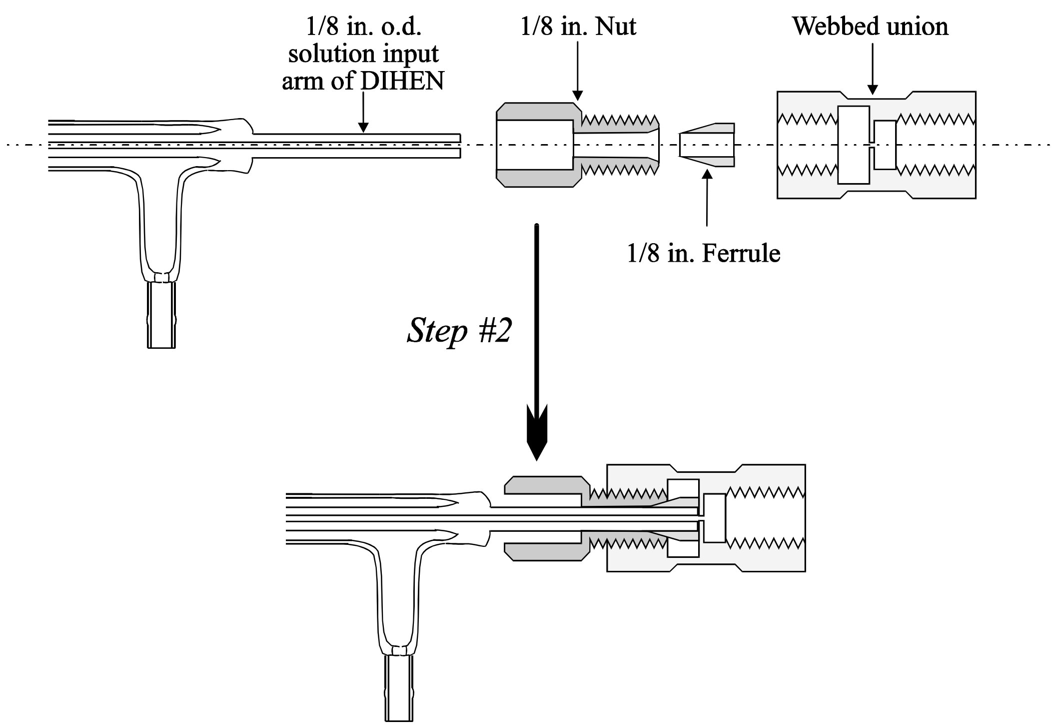


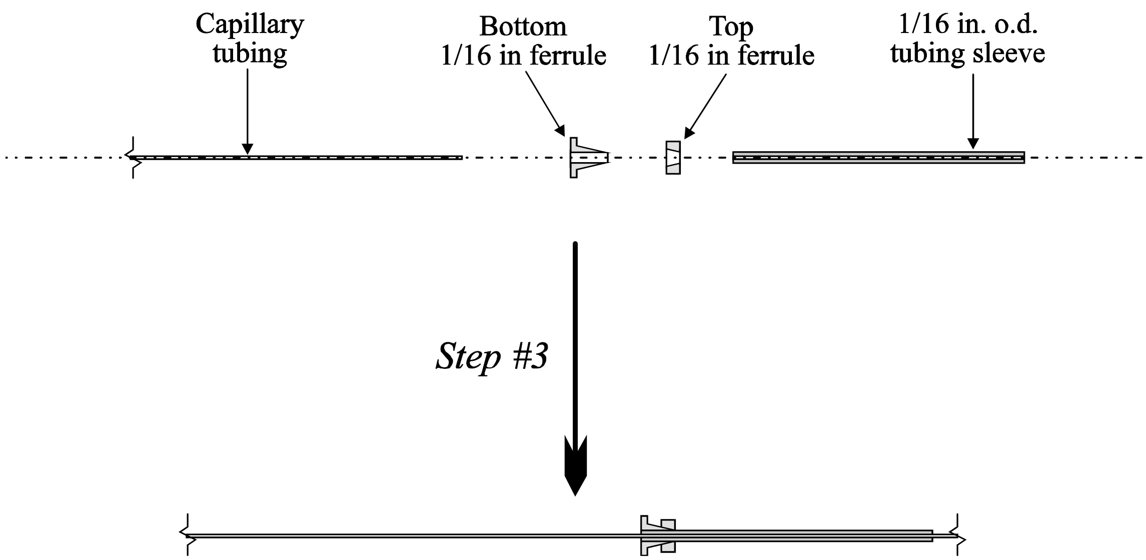
Figure 4. Schematic diagram of SB Fittings Assembly (Fit Kit #1-Micro). Using this kit, one can substantially reduce the dead volume of the DIHEN.

Step #1 - *Trim the capillary tubing*. To achieve the lowest dead volume, use the shortest length of capillary tubing. Determine the desired length of capillary tubing extending from the back of the nebulizer to the solution delivery system. Add to this length the distance from the capillary taper to the end of the nebulizer (approximately 15 cm). Whatever value you obtain, allow an additional 5 cm of capillary tubing for subsequent trimming.

Step #2 - *Connect the union assembly to the DIHEN*. Gently slide the 1/8-in. nut over the solution input arm of the DIHEN. Place the yellow 1/8-in. ferrule over the solution input arm, so that the wide end of the ferrule is flush with the end of the solution input arm. Next, screw the webbed union onto the back of the DIHEN, just to the point where the union is snug. **Caution:** please do not over-tighten or you may break the solution input arm of the nebulizer!

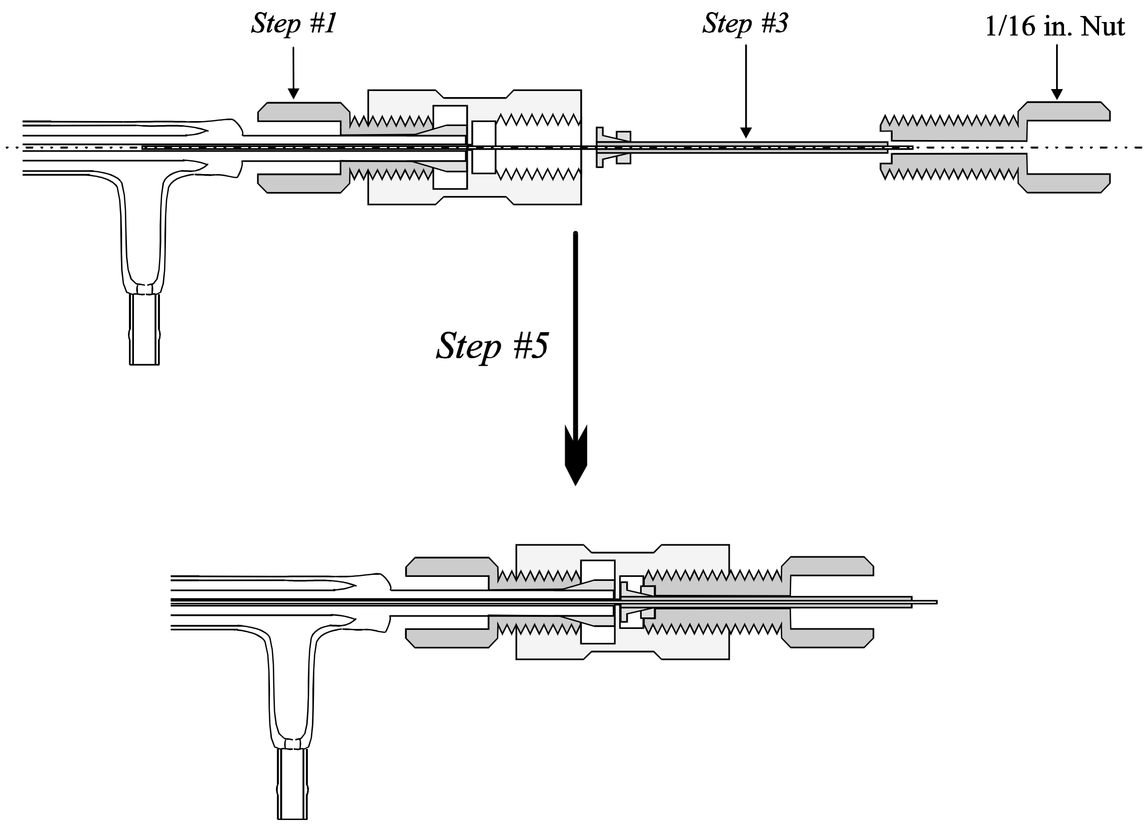


Step #3 - *Secure the capillary tubing inside of the tubing sleeve.* Thread the capillary tubing through the 1/16-in. o.d. tubing sleeve approximately 1 cm longer than the desired length (from capillary taper to the end of the nebulizer solution inlet). Next, slide the crimping ferrules over the end of the tubing sleeve which will join the webbed union. Holding the bottom ferrule flush with the end of the tubing sleeve, press the ferrules together until the capillary tubing is firmly held within the tubing sleeve. **Note:** this may be difficult at first, but becomes routine rather quickly.

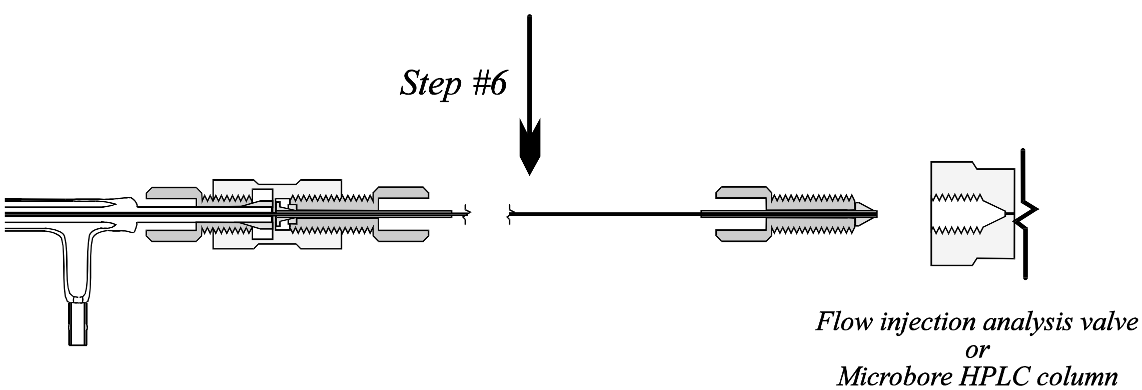


Step #4 - *Insert the capillary tubing into the DIHEN.* Thread the capillary tubing through the hole in the webbed union, to the point where the capillary tubing in snug in the taper of the DIHEN solution capillary. At this point, the bottom ferrule on the tubing sleeve probably does not mount flush with the webbed union (because of the additional 1 cm of capillary tubing). Remove the capillary tubing from the DIHEN and using a clean razor blade, trim a small piece off the end of the capillary tubing. Repeat this procedure until the capillary tubing is snug inside of the DIHEN capillary taper, and the tubing sleeve ferrule is mounted flush with the inside of the webbed union.

Step #5 - *Complete the assembly*. Simply slide the 1/16-in. nut over the opposite end of the capillary tubing and screw this into the union. There is a recess in this nut which should fit firmly over the top ferrule on the tubing sleeve.



Step #6 - *Interfacing the DIHEN with µFIA or µHPLC*. This step is only necessary if you wish to interface the DIHEN with microscale flow injection analysis or microbore high performance liquid chromatography. An additional tubing sleeve and ferrule assembly can be placed on the other end of the capillary tubing for interfacing to *µ*FIA valves or *µ*HPLC columns. The actual tubing sleeve and ferrule should be selected for compatibility with the particular *µ*FIA or *µ*HPLC equipment.



APPENDIX

MAINTENANCE TIPS FOR USERS OF THE MEINHARD® DIHEN

Properly maintained, the DIHEN should yield stable performance indefinitely. However, failure to apply a few simple preventive measures can lead to obstructed gas and liquid passages in the nebulizer which can seriously impair operation. We recommend that you follow the maintenance tips outlined here for long-lasting and trouble-free performance. Refer to Figure 1 above for nebulizer configuration.

Should the DIHEN become clogged, please refer to our website under "Maintenance Tips," which has methods for nebulizer recovery.

On the internet at **www.meinhard.com**

PREVENTATIVE MEASURES

Blockage in the nebulizer is caused generally by either particulate matter (either in the sample solution, or in the carrier gas) or from chemical deposits. It normally occurs in the nozzle where the flow passages become extremely small. Constriction is greatest in the annular gas channel between the tip of the capillary and the taper of the nozzle. This annular gap can be as small as 10-15 µm.

Tip #1. *Filter the carrier gas*. Install low-impedance in-line gas filters to prevent particles from being carried into the nebulizer and lodging in the gas annulus. This is especially important when polytetrafluoroethylene (PTFE-Teflon®) tape has been used in the gas line plumbing. It is possible for shreds of this tape to become wedged in the gas annulus and consequently results in drastic reductions in performance. For the same reason, avoid using PTFE or other friable sealants at the gas connection to the nebulizer.

Tip #2. *Filter the sample.* The sample capillary is more tolerant of particulate matter than the gas annulus. We suggest, however, that you filter or centrifuge the sample if the solids are not of analytical importance. Particulates and colloids of a polar nature such as silica, peptides, polyvalent metal hydroxides and others tend to build up on the (polar) glass and impede the fluid flow. In some instances, you can prevent deposition by adjusting the pH of the suspension away from its (presumed) isoelectric point.

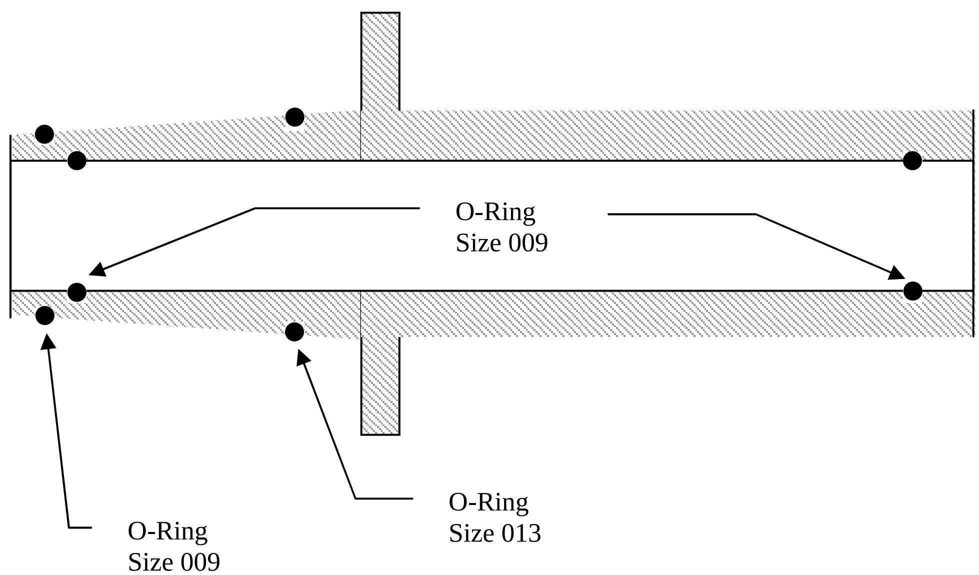
Tip #3. *Rinse your nebulizer*. It is especially important to rinse the nebulizer before turning the gas off. Depending on the chemistry of your samples it may also be advisable to rinse periodically throughout the testing. Solids may deposit in the nozzle as sample solvent evaporates, further constricting the flow passages and reducing the analytical signal. Rinsing will minimize or eliminate these deposits. Follow the testing of any salt solution promptly with a chemically compatible rinse consisting only of volatiles (this is not as necessary in FIA systems.) A low-pH (acidic) sample should be followed by a low-pH rinse; a high-pH sample by a high-pH rinse; an organic sample by an appropriate solvent. Finally, rinse with DDW and/or isopropyl alcohol. Allow the nebulizer to dry before turning off the gas. Also make sure that the liquid feed is disconnected or arranged so as to prevent siphoning into the nebulizer while the gas is off.

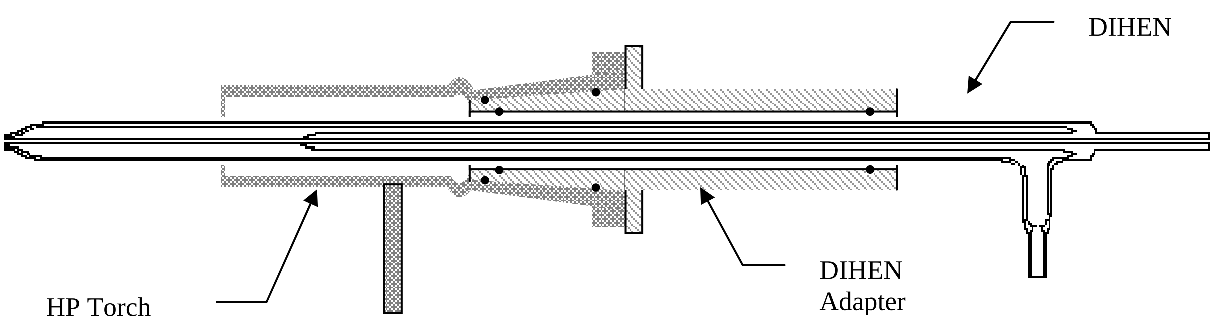
Tip #4. ***Do NOT use ultrasonic cleaning!*** Resonance vibrations may be set in the capillary causing it to bounce against the inside of the nozzle and chip. Nebulizer performance can decline severely as a result.

DIHEN ADAPTERS

Agilent 4500 and 7500

(Drawings not to scale)

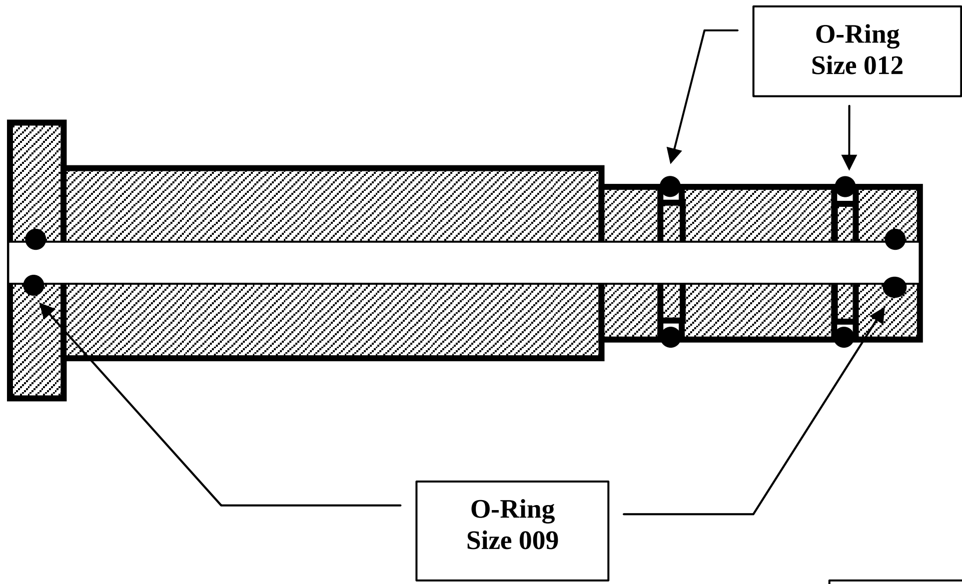


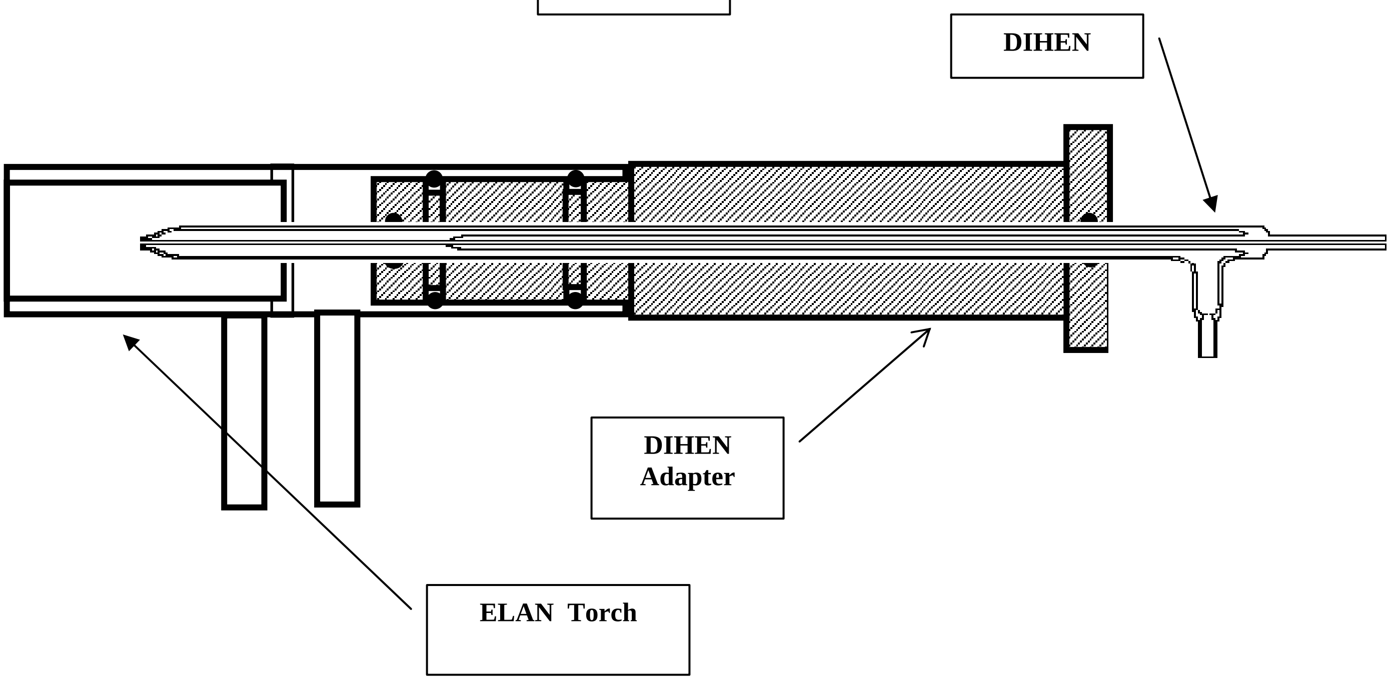


NOTES: DIHEN adapter is to be held to the demountable torch by a plastic joint clamp (Blue, KECK No.19).

ELAN 5000/6000/9000/DRC/DRC II

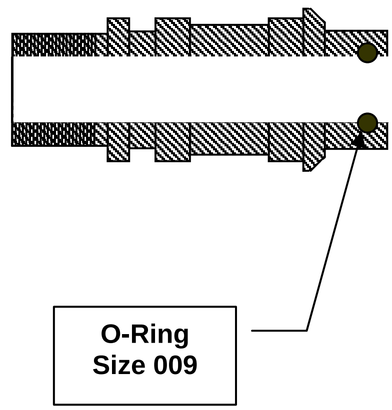
(Drawings not to scale)

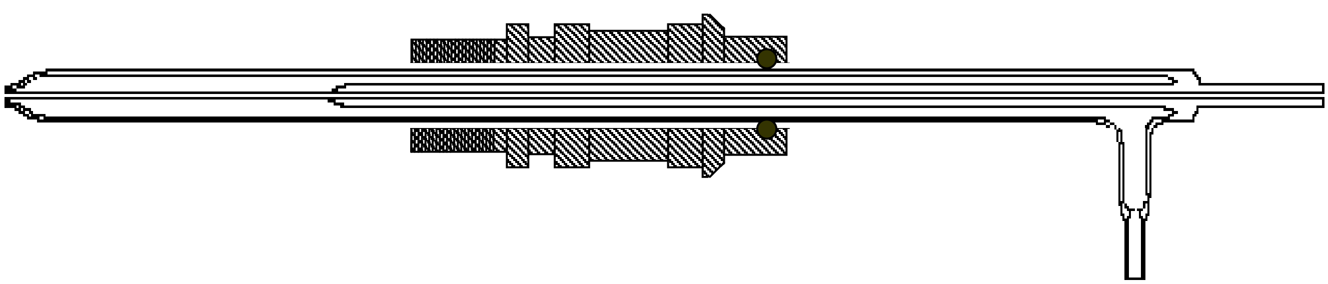




OPTIMA 2000/4000/5000 TORCH

(Drawings not to scale)

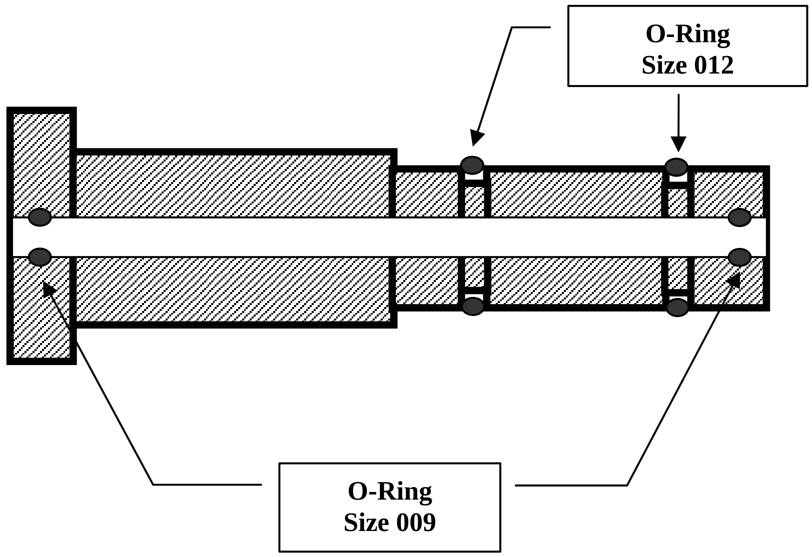


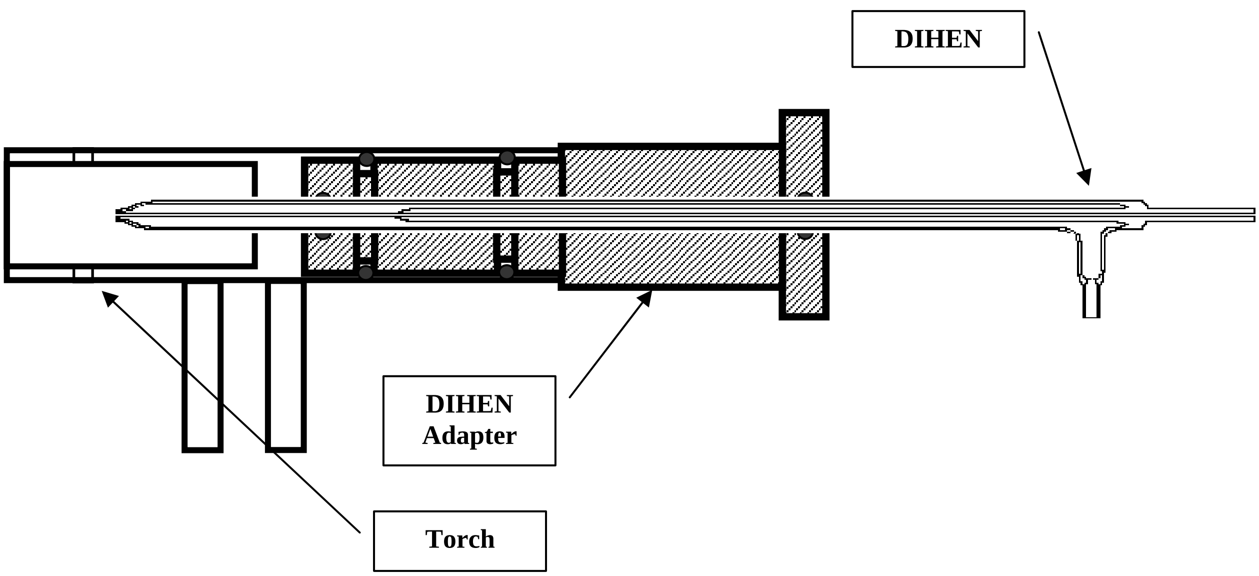


Note: the locking nut, o-ring, and washer must be transferred from the standard injector support.

DIHEN OPTIMA 3000 DV ADAPTER

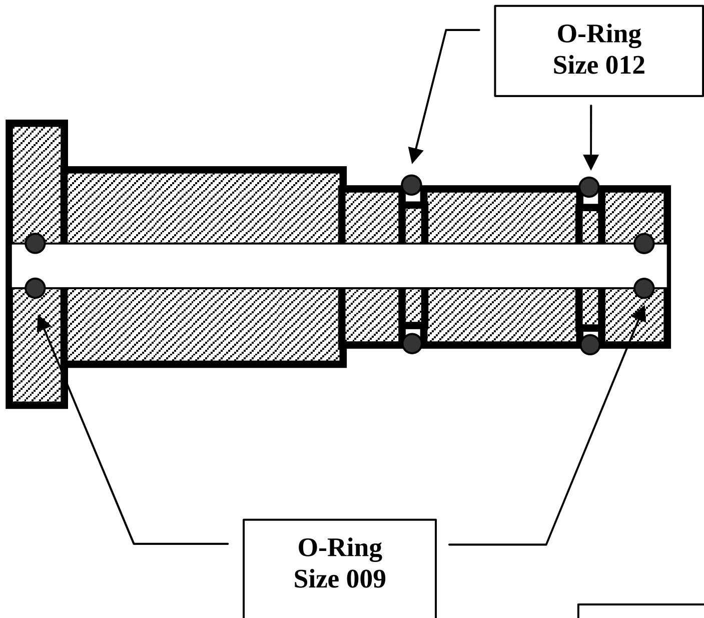
(Drawings not to scale)

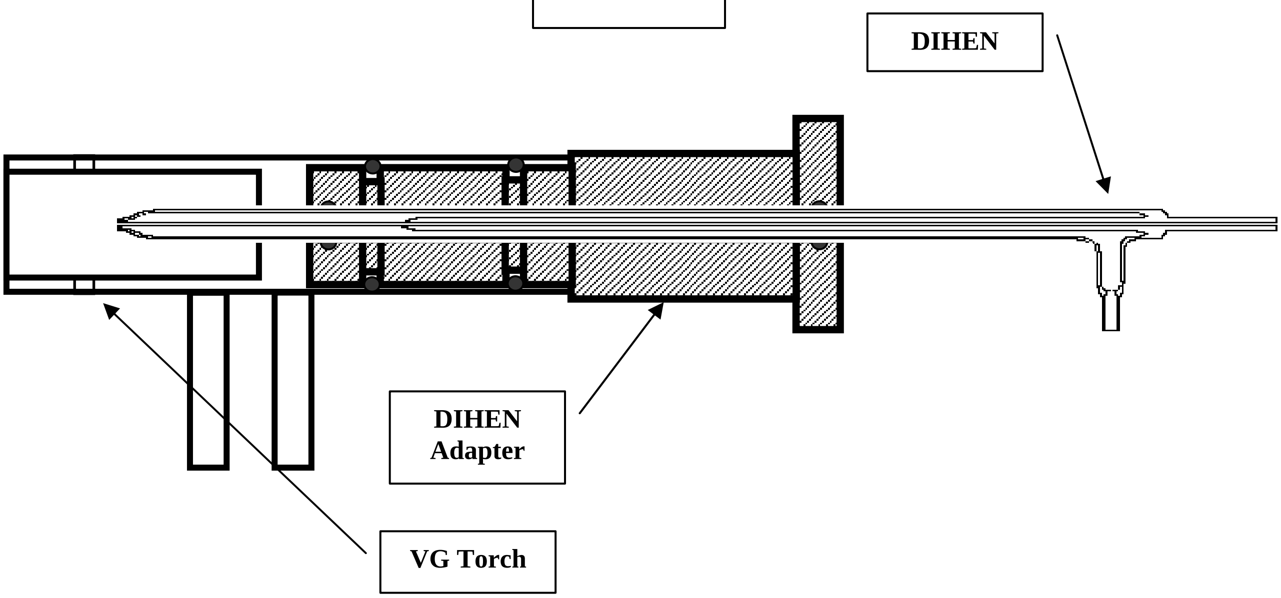




ADAPTER for Thermo VG TORCH

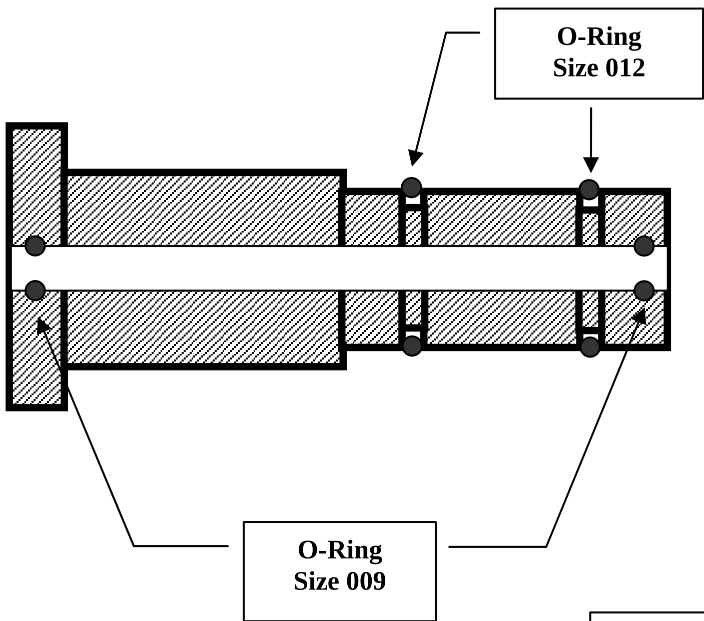
(Drawings not to scale)

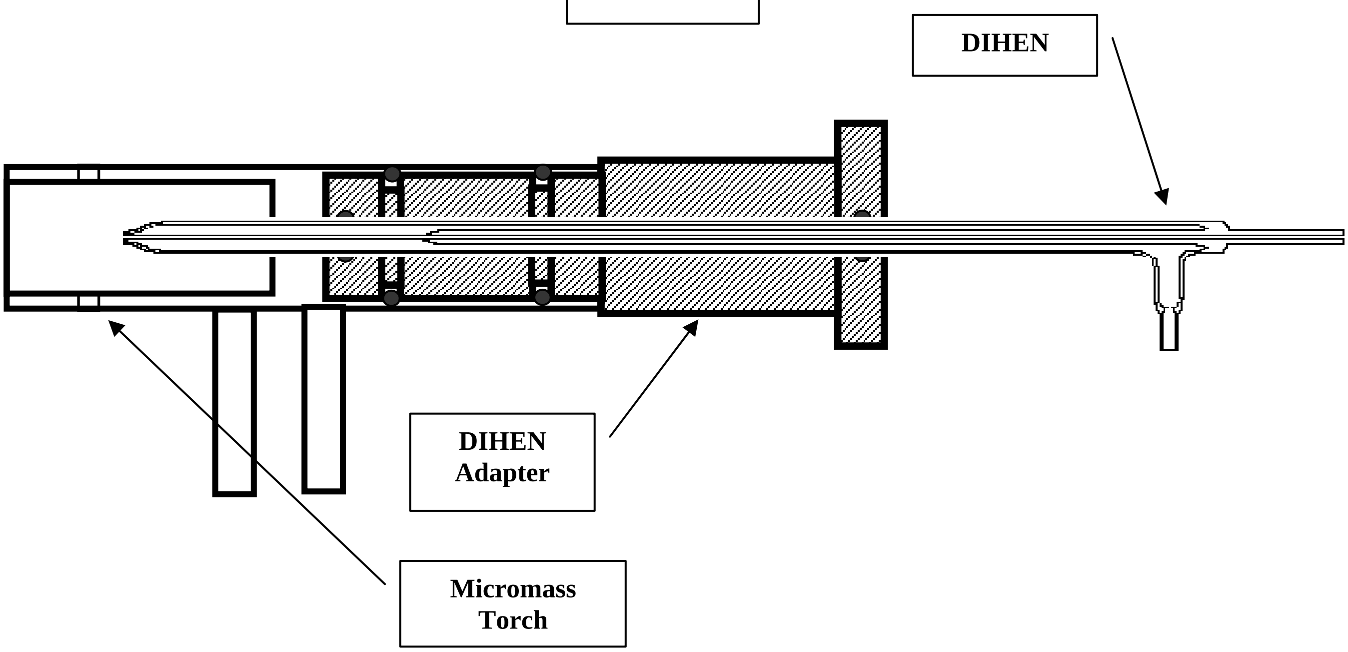




ADAPTER for MICROMASS/GV

(Drawings not to scale)





REFERENCES

i.DIHEN J. A. McLean, H. Zhang, and A. Montaser, "A Direct Injection High Efficiency Nebulizer for Inductively Coupled Plasma Mass Spectrometry," *Anal. Chem*. 70, (1998) 1012-1020.

ii.DIHEN J. A. McLean, M. G. Minnich, L. A. Iacone, H. Liu, and A. Montaser, "Nebulizer Diagnostics: Fundamental Parameters, Tools, and Techniques on the Horizon," *J. Anal. At. Spectrom.* 13, (1998) 829-842.

iii.DIHEN J. Singh, J. A. McLean, D. E. Pritchard, A. Montaser, and S. R. Patierno, "Sensitive Quantitation of Chromium-DNA Adducts by Inductively Coupled Plasma Mass Spectrometry with a Direct Injection High Efficiency Nebulizer," *Toxicological Sciences* (in press).

iv.HEN H. Liu and A. Montaser, "Phase-Doppler Diagnostic Studies of Primary and Tertiary Aerosols Produced by a High-Efficiency Nebulizer" *Anal. Chem*. 66, (1994) 3233-3242.

v.HEN S-H. Nam, J-S. Lim, and A. Montaser, "High-Efficiency Nebulizer for Argon Inductively Coupled Plasma Mass Spectrometry," *J. Anal. At. Spectrom.* 9, (1994) 1357-1362.

vi. S. C. K. Shum, S. K. Johnson, H-M. Pang, and R. S. Houk, "Spatially Resolved Measurements of Size and Velocity Distributions of Aerosol Droplets from a Direct Injection Nebulzier," Appl. Spectrosc. 47, (1993) 575-583.

vii. A. Montaser, M. G. Minnich, J. A. McLean, H. Liu, J. A. Caruso, and C. W. McLeod, "Sample Introduction in ICPMS," In *Inductively Coupled Plasma Mass Spectrometry*, A. Montaser, Ed., Wiley-VCH, New York, (1998) 83-264.

viii. A. Montaser, M. G. Minnich, H. Liu, A. G. T. Gustavsson, and R. F. Browner, "Fundamental Aspects of Sample Introduction in ICP Spectrometry," In *Inductively Coupled Plasma Mass Spectrometry*, A. Montaser, Ed., Wiley-VCH, New York, (1998) 335-420.

ix. S. Greenfield and A. Montaser, "Common RF Generator, Torches, and Sample Introduction Systems." in *Inductively Coupled Plasmas in Analytical Atomic Spectrometry*, 2nd Ed., A. Montaser and D. W. Golightly, Eds., Wiley-VCH, New York, (1992) 187-247.

x. A. G. T. Gustavsson, "Liquid Sample Introduction into Plasmas." in *Inductively Coupled Plasmas in Analytical Atomic Spectrometry*, 2nd Ed., A. Montaser and D. W. Golightly, Eds., Wiley-VCH, New York, (1992) 679-720.

xi. B. L. Sharp, "Pneumatic Nebulizers and Spray Chambers for Inductively Coupled Plasma Spectrometry, A Review, Parts 1 and 2," *J. Anal. At. Spectrom.* 3, (1988) 613-652 and 939-963.

xii. R. F. Browner, "Fundamental Aspects of Aerosol Generation and Transport." In *Inductively Coupled Plasma Emission Spectroscopy, Part II*, P. W. J. M. Boumans, Ed., Wiley, New York, (1987) 244-288.

Questions and Answers on the Application of DIHEN and LB-DIHEN in ICP Spectrometry

Please ask your colleagues to FIRST read the Instruction Manual available from Meinhard Glass Products BEFORE using the DIHEN or LB-DIHEN. Importantly, one has to first operate the ICP system with the "DIHEN shell" or "dummy nozzle" before using the DIHEN. This is to gain experience and prevent melting the DIHEN or the LB-DIHEN!

Here are frequently asked questions with answers:

Question 1:

We are trying to couple the DIHEN to an ICPMS from Agilent Technologies (Hewlett Packard) Model 4500. The Ar supply available in our lab provides us with a maximum pressure of 6 bar. Is it enough to operate the DIHEN? (We believe that micro-nebulizers such as the HEN require pressures of about 8 bar).

Answer to Question 1:

You are correct that devices like the HEN require ~8 bar when used at 1 L/min, but the DIHEN typically operates at 0.15 to 0.25 L/min for optimal sensitivity which is ~50 psig or ~3.5 bar. The DIHEN should work fine on your system (6 bar ~87 psig). The large bore-DIHEN (LB-DIHEN) operates at even lower pressures and is also good for analysis of solutions with high amounts of dissolved solids or slurries.

Question 2:

Considering that the position of the nebulizer in the demountable torch seems to be a critical parameter, where exactly do you think the tip of the DIHEN should be positioned?

Answer to Question 2:

Yes, the position is important. The DIHEN or the LB-DIHEN should be approximately 2 mm below the intermediate tube of the ICP torch. For the first time user, the “DIHEN shell” or "dummy nozzle" should be used for practice igniting the plasma.

Question 3:

With the standard Meinhard nebulizers, we are using the following instrumental parameters: Intermediate gas flow 1 L/min; outer gas flow 15 L/min; RF power 1300 W. Do you think that some of these parameters are very different from the usually optimum conditions for the DIHEN?

Answer to Question 3:

The DIHEN or the LB-DIHEN typically has quite a distinct optimum condition compared to nebulizers used with spray chambers. This is because a much higher solvent load is injected into the plasma. The outer gas flow rate should not change much, but a higher intermediate flow (~1.4-1.6 L/min) provides better results because the plasma is pushed away from the nebulizer tip. In addition, a higher RF power is required because of the increased solvent load. For the Elan

6000 ICPMS, typically 1500 W is used, while on high-resolution instruments such as the Element ICPMS, ~1100-1200 W is applied. As with the other parameters, this should be optimized on your system.

Question 4:

We are using a peristaltic pump for sample introduction (flow rate of ~50 μL/min). Unfortunately, the flow obtained with the peristaltic pump is not completely smooth and it presents small pulses. These pulses don't seem to cause many problems with conventional Meinhard nebulizers operated at higher solution uptake rates. Do you think more problems are expected when using the DIHEN? Which pump should be used?

Answer to Question 4:

You are correct. The peristaltic noise is more severe at low solution flow rates. A syringe pump is typically utilized for very low flow rates (<40 μL/min), but a peristaltic pump can be used at flow rates of 80-100 μL/min (typically optimum sensitivity). Two things are performed to minimize the noise. First, please use very narrow bore peristaltic tubing so that the roller rotation is very fast. Either 0.015 in id (orange-green) or 0.0075 in id (red-orange) tubing seem satisfactory. Second, a microfitting kit (SB Fitting Assembly, Fit Kit #1 Micro, from Meinhard Glass Products) should be used to reduce the dead volume of the DIHEN (see the DIHEN Instruction Manual). This reduces the dead volume to <15 microliter, and also acts to damp peristaltic noise.

Question 5:

We have installed the DIHEN on our PlasmaQuad ICPMS with the assistance of a VG Service Engineer. We had a good plasma ignition, but unfortunately, the tip of the DIHEN was too close to the plasma and it melted during the tuning process. Do you think that the glassblower may grind the tip very carefully to fix it?

Answer to Question 5:

For the first-time user of the DIHEN (or LB-DIHEN) with any ICP instrument, the "DIHEN shell" or "dummy nozzle" should be used for practice in igniting the plasma (see the Instruction Manual). The damaged DIHEN should be returned to Meinhard Glass Products for possible repair. Grinding the tip will permanently damage the DIHEN.

Question 6:

We have installed a DIHEN on our PlasmaQuad ICPMS. We had a good plasma ignition at 1400 W, but the plasma started to burn the nebulizer tip at 1350 W. To reduce burning, the nebulizer gas flow was increased, but the plasma collapsed and melted the DIHEN tip at a nebulizer gas flow of approximately 0.05 L/min. How should we prevent another melt down with a new DIHEN?

Answer to Question 6:

The DIHEN requires a very low nebulizer gas flow (0.15 L/min to 0.25 L/min) for optimal operation. Perhaps you neglected to utilize an intermediate gas flow at an appropriate level (typically 1.0 to 1.2 L/min). The ICP torch requires three gas flows for stable operation: an outer gas flow (or the coolant flow or plasma gas flow), an intermediate gas flow (or auxiliary gas flow), and a nebulizer gas flow. The outer gas flow sustains the plasma, normally at ~15 L/min argon. The intermediate gas flow passes through the intermediate tube of the ICP torch at a rate of about 1.0 to 1.2 L/min. In most ICP instruments, the intermediate gas flow must be used not only to ignite the plasma but also during normal operation. This is essential to push the hot bottom of the plasma away from the injector tube of the torch (or in your case, the DIHEN tip); otherwise the nebulizer will be gradually plugged. For further assistance, please provide details about the ICP operating conditions used and the plasma shut down process.

Question 7:

My associates broke the DIHEN by rough handling. The solution inlet at the backside of the DIHEN was broken. Our glassblower repaired the DIHEN by fixing a GCMS capillary into the solution inlet tube.

Answer to Question 7:

Just like any other micronebulizer, the DIHEN (or LB-DIHEN) must be handled with care. In general, we recommend returning the damaged DIHEN to Meinhard Glass Products for repair.

Question 8:

We plan to use the DIHEN with an Elan 6000 ICPMS. Would this instrument tolerate direct injection of sample? What are exact gas flow rates and RF power at different stages of ignition and operation of this instrument with the DIHEN or LB-DIHEN?

Answer to Question 8:

The Elan 6000 ICPMS instrument is equipped with a free-running generator and a balanced load coil circuitry. The ignition and operation of the ICP are simpler compared to other ICPMS instruments equipped with a crystal-controlled generator and impedance matching network.

The ignition procedure for Elan 6000 ICPMS is computer controlled. We begin with a gas purge. Under normal operation, there is no operator control over the intermediate and outer gas flow rates. These are determined by the regulated back-pressure of the gas. The back-pressure is set to 51 $\pm$ 1 psig (recommended by Sciex) which provides an intermediate gas flow rate of 1.2 L/min and an outer gas flow rate of 15 L/min (manufacturer specifies both of these flows to be $\pm$ 10%). We usually have a very clean ignition, provided that there are no air leaks in the system.

The nebulizer (or injector) gas flow rate is also under instrument control. During ignition, the flow rate is set to 1 L/min to purge the nebulizer while the RF generator is warmed. Several seconds before the ignition, the flow rate is reduced to 0 and then raised to the operator-set flow rate after the plasma is ignited.

When operating the DIHEN on the Elan 6000, we usually use an external mass flow regulator and light the plasma while continuously introducing nebulizer gas at a flow rate between 0.2 to 0.25 L/min without introducing any solution. However, the instrument-controlled nebulizer gas line has been used with the LB-DIHEN. In this case, the nebulizer gas is reduced to 0 during ignition as stated earlier. No difficulty in lighting the plasma is experienced with both scenarios.

In igniting the plasma with a DIHEN, an RF power of 1200 W is applied. Occasionally, the plasma does not stay lit after ignition (it appears to "blow away", presumably by the nebulizer gas) in which case an RF power of 1300 W is used for ignition. After the plasma is ignited and mass spectrometer interface gate opens, the RF power is increased to normal operating mode (1500 W). At this point, solution is introduced into the DIHEN for direct injection into the plasma.

Question 9:

We have a new ICPMS manufactured by Nu Company. Would it be possible to use the DIHEN with this instrument?

Answer to Question 9:

The DIHEN can be used with any ICP instrument. For a new ICPMS/AES instrument, the task is often simple with the assistance of the manufacturer engineer or someone who is aware of the sequence of automatic operation. For the Nu ICPMS instrument, the nebulizer gas flow turns off a few seconds before plasma ignition, but the back pressure in the nebulizer line requires a relatively long time (10-15 seconds) to dissipate through the very small DIHEN nozzle, and this flow is sufficient to cause problems in plasma ignition and operation. By manually purging the nebulizer line and turning the nebulizer flow off early, the operator can achieve a very low nebulizer pressure (<4psig) which would allow the plasma to ignite.

Question 10:

We read the paper on Direct Injection High Efficiency Nebulizer (Anal. Chem. 70, 1012-1020 (1998) with interest. We are in the process of purchasing a multi-collector ICPMS (MM Isoprobe, etc.). One of the key projects we wish to pursue is high-precision (0.002 to 0.005%) Fe isotope ratio measurement. We have conducted extensive tests on Micromass, VG Elemental, and Nu Instruments. Clearly, several other options for removing spectral interferences exist, namely, using a quadrupole collision cell and/or cool plasma.

Our goal is to run very small samples, and hence the efficiency of the DIHEN is of interest to us. In addition, we have found memory effects with other nebulizers such as the MCN-6000, especially when there are large changes in isotopic compositions between samples. Our questions are: 1) Have you explored the DIHEN using cool plasma to see the level of ArN^+ and ArO^+? 2) Do you know of anyone has tried the DIHEN on a collision-cell-based instrument? 3) What are the drawbacks of the DIN vs. the DIHEN? 4) What do they cost?

Answer to Question 10:

We have found the DIHEN to be a good alternative to both DIN and conventional nebulizer-spray chamber combinations, especially in the analysis of very small (μL) size samples.

In reference to Fe and cool plasma, the DIHEN actually works very easily in establishing a cool plasma condition on Elan 6000 ICPMS. The DIHEN has also been explored on double-focussing instruments such as the Element ICPMS. Work is in progress in coupling a DIHEN to a Perkin-Elmer ELAN 6100 DRC-ICPMS. This instrument, a quadrupole dynamic reaction cell, has proven effective in the eliminating isobaric interferences due to ArN^+ and ArO^+.

In comparing the commercial DIN (CETAC Technologies) and the DIHEN (Meinhard Glass Products), two primary issues should be considered: simplicity and cost. The DIN is relatively complex, is approximately $20,000, requires a high pressure solution delivery pump, and optimization of many variables in addition to standard plasma operating conditions (e.g. auxiliary nebulizer gas, capillary position). The DIHEN is a simple one-piece construction, is sold for $2,000, and does not require a high-pressure pump. Indeed, natural aspiration of solutions provides very good results. Both the DIN and the DIHEN offer 100% analyte transport efficiency and are suitable for the analysis of very small sample types. The elimination of the spray chamber reduces a number of noise sources and matrix effects. The wash-in and wash-out characteristics of both the DIN and the DIHEN are far superior to the nebulizer-spray chamber combination, mainly because the dead volume is much lower. A drawback of both designs is that capillary blockage is encountered with the analysis of high levels of total dissolved solids. With a large bore-DIHEN (LB-DIHEN), nebulizer clogging is minimized. The DIHEN or the LB-DIHEN also provides greater absolute sensitivity, which is 10-30 times higher than that obtained by conventional devices.

Question 11:

We are trying to get an idea of the relative sensitivity of the DIHEN. It is difficult to compare count rates using a quadrupole ICPMS with magnetic sector ICPMS (MS-ICPMS), which really measures ion currents in Faraday collectors over periods of 10 minutes. Converting the ion currents for MS-ICPMS to count rates, we get the following data for Mn, Fe, Co:

Standard low-flow nebulizer and spray chamber (100 μL/min): 4x10^8 cps/ppm

MCN-6000 (50 μL /min): 2x10^9 cps/ppm

Our goal is to obtain the highest count rates with the smallest total sample consumed (not necessarily volume, but total mass of Fe consumed, for example). Using the above data as a guide to the MS-ICPMS, please give us a feel for the equivalent count rates (and at a given flow rate) for the DIHEN?

Answer to Question 11:

It is difficult to compare relative sensitivity obtained on a quadrupole vs. a sector instrument. Sensitivity on the sector instrument largely depends on the resolution. At a resolution of 300, sector instruments typically provide relative sensitivity, which is in most cases at least 10 times higher than what is obtained on the quadrupole instruments.

Here are some relative sensitivity values obtained on the quadrupole instrument in comparison with both a MicroMist (micronebulizer)-coupled with a low volume (20 mL) spray chamber and a conventional cross-flow nebulizer with a Scott-type spray chamber.

Results from Elan 6000 ICPMS:

^{238}U- (From Anal. Chem. 71, 1999, 3077-3084)
DIHEN (100 μL/min): 2.3 x 10^8 cps/ppm
MicroMist (100 μL/min): 4.5 x 10^7 cps/ppm
Crossflow (1 mL/min): 6.0 x 10^7 cps/ppm

^{59}Co- (From Anal. Chem. 70, 1998, 1012-1020)
DIHEN (85 μL /min): 5.6 x 10^7 cps/ppm
Crossflow (100 μL /min): 5.7 x 10^6 cps/ppm
Crossflow (1 mL/min): 2.6 x 10^7 cps/ppm

^{55}Mn- (From Anal. Chem. 70, 1998, 1012-1020)
DIHEN (85 μL /min): 6.5 x 10^7 cps/ppm
Crossflow (100 μL /min): 7.2 x 10^6 cps/ppm
Crossflow (1 mL/min): 3.2 x 10^7 cps/ppm

In terms of relative sensitivity, the DIHEN performs similarly to or much better than most other nebulization devices. In terms of absolute sensitivity, the DIHEN is a factor of 10 to 30 times better than the nebulizer-spray chamber arrangement in many cases.

The DIHEN offers the highest signal for the least amount of test sample. It provides good sensitivity (on the order of 10^6 to 10^7 cps/ppm for most elements), even when operated at only 1 μL /min. For instance, the relative sensitivity for ^{238}U is 2.3 x 10^8 cps/ppm at 100 μL /min. At 1 μL/min, the relative sensitivity is still 1.8 x 10^7 cps/ppm. In terms of absolute sample consumed, this attribute is a tremendous advantage. However, precision is deteriorated at very low uptake rates, from 0.5 to 2.3 %RSD for ^{238}U at 100 μL /min and 1 μL /min, respectively.

Question 12:

We are unable to acquire sensitivities near those reported in first article on the DIHEN-ICPMS (Anal. Chem. 70, 1012-1020 (1998) although we have kept the parameters very similar to those listed.

Answer to Question 12:

If the nebulizer is not clogged, low sensitivity is often attributed to incorrect values for three parameters: 1) the x-y-z position for the torch/DIHEN is not optimized; 2) the nebulizer gas flow rate is too high; and 3) the RF power is too high.

Question 13:

The plasma hisses audibly when we use the DIHEN and does not when conventional sample introduction systems are used. Is this normal?

Answer to Question 13:

Yes, hissing has actually been noted with the other direct injection nebulizers as well. Audible hissing is attributed to the injection of more solvent from the primary aerosol (rather than the tertiary aerosol) into the plasma. When the solution delivery is off, the plasma will remain silent until the solution is turned on again. When using a peristaltic pump, however, a hissing sound may still be heard even with the solution delivery turned off due to the natural aspiration.