

Instrument: GDS900/GDS950

Wire and Rod Analysis by Glow Discharge

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Key Words: Atomic Emission Spectrometer, GDS950, GDS900, Wire, Rod, Holder

Introduction

Glow Discharge Spectrometry (GDS) is an analytical method for the direct determination of the elemental composition of solid samples. A prepared flat sample is mounted on the glow discharge source, then the source is evacuated and backfilled with argon. A constant electric field is applied between the sample (cathode) and the electrically grounded body of the lamp (anode). These conditions result in the spontaneous formation of a stable, self-sustained discharge, which is called a glow discharge.

Since each element has a unique electronic configuration, every element can be identified by its unique spectrochemical signature or emission spectrum.

A spectrometer is used to measure the emission signals from the glow discharge. Since the number of photons emitted by each element is proportional to its relative concentration in the sample, analyte concentrations can be deduced by calibration with reference samples of known composition.

Alternative techniques, such as ICP, require complete sample digestion via acid into solution for introduction into the plasma. This technique is very time consuming, requiring complex wet chemical dilutions, and generates significant hazardous waste. Glow discharge offers a faster, safer, more direct way to analyze samples.

Application

Conductive solid materials can be sputtered if two sample-related conditions are met.

1. The sample face must be solid, smooth, and flat enough to establish a vacuum seal between the lamp and the sample with an o-ring.
2. A path for the current to flow between lamp face and sample must exist outside of the o-ring seal. Samples therefore need to be slightly larger than both the inside anode and o-ring diameter.

These conditions have historically limited glow discharge to larger solid samples than wires and rods, but with the use of specialized sample holders, the glow discharge technique can be applied to wires and rods that are too small to meet the physical constraints. This Application Note outlines the steps necessary to analyze wires and rods with the GDS900/GDS950 with various sample holders. The holders provide a means to bundle wires or fit rods, providing enough surface area to create a vacuum seal on the o-ring and to complete the electrical circuit while the sample is held directly over the anode.



Materials & Applications

Lamp Options

Three lamp/anode combinations exist to help fit your specific needs. Figure 1 shows the three anodes and two o-ring sizes available.

1. The 4/14 Lamp with a 4 mm anode and 14 mm blue o-ring is recommended for analysis of all wire sample diameters. Large rods, greater than 12 mm in diameter, can be mounted directly on the lamp. Small diameter wires require the aid of one of the sample holders described in this note.
2. The 2/14 Lamp can be fitted with an optional 2 mm anode which allows analysis of 3 to 4 mm rods/wires and parts without forging using a holder. Only the reamer assembly and anode need be changed, the rest of the lamp parts are common with the standard 4/14 mm lamp assembly. The o-ring diameter is not changed.
3. The optional 2/9 Lamp is a 2 mm anode and 9 mm red o-ring. It can be used to analyze small parts between 8 and 12 mm directly on the lamp. All the parts of this lamp are unique and not interchangeable with the standard lamp. Refer to Table 1 for specific diameters.

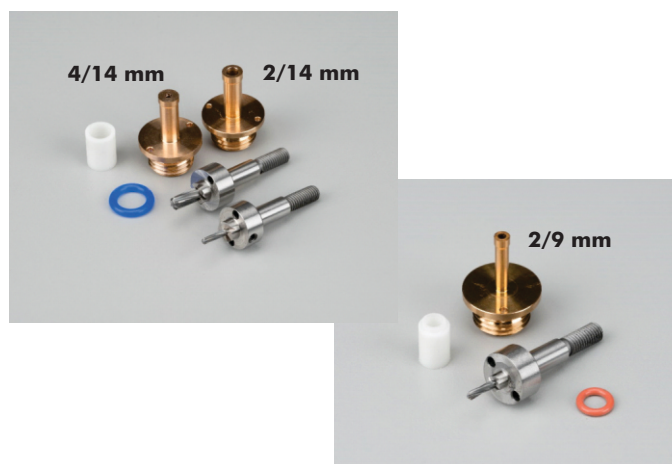


Figure 1. Reamers, anodes, sleeves, and o-rings.

Wire Holder Description

LECO offers two options of special wire holders for various wire diameters <12 mm. There are two wire holders available. Sample Holder Assembly 691-103-425 (Figure 2) comes pre-drilled with a 3 mm pilot hole. It can be drilled to fit larger-sized wires or rods (up to 12 mm) and is reusable for that size wire. A set screw holds the wire in place while another screw with an o-ring makes an air tight seal.

Wire Holder 833-101-139 (Figure 3) is used for wires less than 3 mm in diameter. The wires need to be cleaned, cut, and bundled together as a group, then forged into place. The forging procedure is described in this note. Once the sample is forged then the size is more than adequate to analyze using the 4/14 mm lamp.

Grinding is required to achieve adequate flatness. Grinding requirements are described in the Sample Preparation section of this note. These holders can be reused by drilling out the old sample. In time, holders will wear due to grinding of the surface and will require replacement.



Figure 2. Sample holder assembly 612-708.



Figure 3. Wire holder assembly 833-101-139.

Table 1 shows ranges of wire diameters, mounting requirements, and optional lamp/anode sizes. The optional 2/9 Lamp can analyze a smaller wire diameter without special mounting, however, as sample diameters become <3 mm this advantage is no longer relevant and the 4 mm lamp becomes the better option. Choice of lamps will depend on wire diameter size most often encountered. If all sizes of wire are expected, then having all the lamp options available should be considered.

Table 1. Wire Diameters And Special Holders Used On Standard Lamp & Small Lamp Options

Wire Diameter	Inside Anode Diameter & Lamp Size		
	4/14 Lamp	2/14 Lamp	2/9 Lamp
≥ 12 mm	Place Sample Directly on Lamp	Place Sample Directly on Lamp	Place Sample Directly on Lamp
8 mm - 12 mm	Sample Holder Assembly 691-103-425 Required	Sample Holder Assembly 691-103-425 Required	Place Sample Directly on Lamp
5 mm - 8 mm	Sample Holder Assembly 691-103-425 Required	Sample Holder Assembly 691-103-425 Required	Sample Holder Assembly 691-103-425 Required
3 mm - 5 mm	Forging into Wire Holder 833-101-139 Required	Sample Holder Assembly 691-103-425 Required	Sample Holder Assembly 691-103-425 Required
≤ 3 mm	Forging into Wire Holder 833-101-139 Required	Forging into Wire Holder 833-101-139 Required; 4 mm Anode Can Be Used	Forging into Wire Holder 833-101-139 required; 4 mm Anode Can Be Used

Rod Mounting and Analysis

Mounting Directly to the 4/14 mm Lamp

Rods ≥12 mm can be surface prepped and mounted directly on the 4/14 mm lamp either on end or by sectioning longitudinally, providing a rectangular surface. Sectioning is advantageous because multiple analyses can be performed without resurfacing. Samples should be prepared using 120-grit or higher silicon carbide abrasive. Figure 4 shows two examples of direct mounting. The left sample could be analyzed directly at its end or after sectioning, whereas the right example show how the o-ring does cover the sample, but would not make electrical contact outside of the o-ring. When sectioned, there was enough surface area to obtain a vacuum seal and form an electrical connection with the lamp.

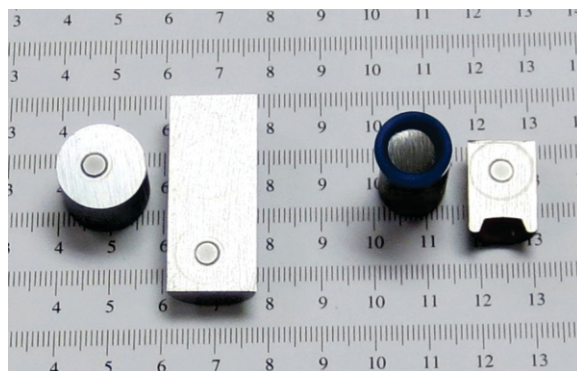


Figure 4. The 4/14 mm lamp direct mount examples.

Mounting Directly to the 2/9 mm Lamp

Wires/rods as small as 8 mm can be mounted directly to the 2/14 Lamp if sectioned lengthwise. The sample shown in Figure 5 would not seal on end using the red o-ring, so it was sectioned lengthwise, providing enough surface area for three analyses.

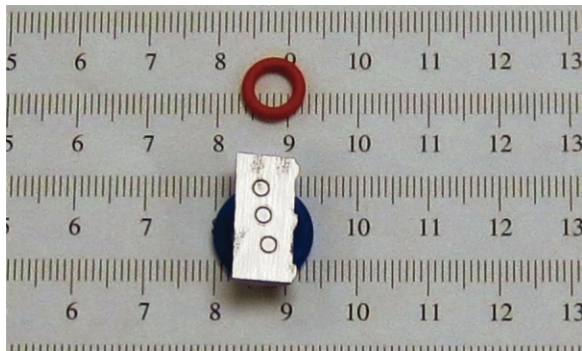


Figure 5. 2/9 Lamp was used for direct mounting and analysis of the sample.

Using the Sample Holder Assembly 691-103-425

The reusable holder comes with a 3 mm pilot hole and can be drilled to fit a larger diameter sample. A set-screw holds the sample in place for analysis. Samples can be exchanged between analyses. The sample should be straightened and cleaned before placing it into the holder. The wire should fit easily into the holder and not forced. The wire should be 10 to 20 mm in length. Place the wire into the holder allowing some to protrude, tighten the set screw. Once the individual section of sample is in place, a quick dry grind will make sure the sample and holder face are both parallel and flat. After analysis, loosen the set screw and tap the holder to remove the sample. The holder will eventually need replacing because of repeated grinding.

Using the Wire Holder 833-101-139

Samples less than 3 mm in diameter can be analyzed by first forging multiple sections of the sample together. Pre-drilled holes are present on both sides of the sample holder, so both sides can be used for sample preparation. The forging process requires physical effort to achieve a well packed sample. Using straight wires will allow for more uniform packing, and will reduce the amount of effort required.

Be sure to have ample material to completely fill the hole in the block. The amount of sample depends upon the diameter of the wire. For example, a 2 mm diameter wire will require approximately 2.5 inches (64 mm) of length while a 1 mm diameter wire will require approximately 10 inches (256 mm) of length.

Annealing

We recommend annealing ferrous-based materials unless you know the wire to be sufficiently soft. Starting at one end, place the wire into the flame until the wire becomes a dull red color; continue to draw the wire slowly through flame along its length. The wire should only be hot for seconds. Let the wire cool in air. Springs can be straightened after annealing. This step can be omitted for already soft materials such as aluminum or copper.

Forging Steps

Refer to Figures 1 through 10 on next page.

1. Anneal the wire if necessary. A Bunsen burner or propane torch will suffice.
2. Abrade the wire with an abrasive pad or file.
3. Clean the wire with fresh reagent grade solvent such as alcohol or acetone to remove organic contaminants. (Be careful not to touch the sample after cleaning.)
4. Clean the inside diameter of the holder as well.
5. Cut the wire to length; use wire holder as gauge.
6. Pack the sections as tightly as possible into the block using tweezers.
7. The few last wire sections fit better if sharpened to a point.
8. Forge using a peening hammer. Tap lightly at first until the wire sections become wedged, then exert more and more force with the hammer.
9. Grind the sample flat using the appropriate media.
10. Using the reamer as a pointer, align the holder on the lamp and analyze.

Sample Preparation

LECO manufactures belt grinders, variable speed polishers, and cut-off saws for metallographic analysis; these are also suitable for polishing and cutting samples. Ferrous-based samples are surface abraded using a 120-grit zirconium oxide dry belt (PN 810-499) while aluminum and other soft materials (Cu, Monel, Ti, etc.) are surface abraded using a 320-grit silicon carbide disk (PN 810-253-PRM) with water. Sectioning rod samples lengthwise was performed using a LECO MSX-205-M2 water-cooled cut-off saw.

Limitations

Not all wire samples are suitable for analysis using the described methodology, such as samples that are too hard or brittle to be forged. Wire diameters that are 0.5 to 0.7 mm or less may not be practical due to the number of sections (>100) required to fill the holder. Coatings should be removed before mounting the sample unless the coating material is taken into account. Filled welding wire is not recommended.

Distinct calibrations are required for 4 mm and 2 mm lamps. A method calibrated with the 4 mm anode can not be used to analyze samples using the 2 mm anode and vice versa. Methods for solid sample analysis, however, are applicable to wire samples of similar composition.

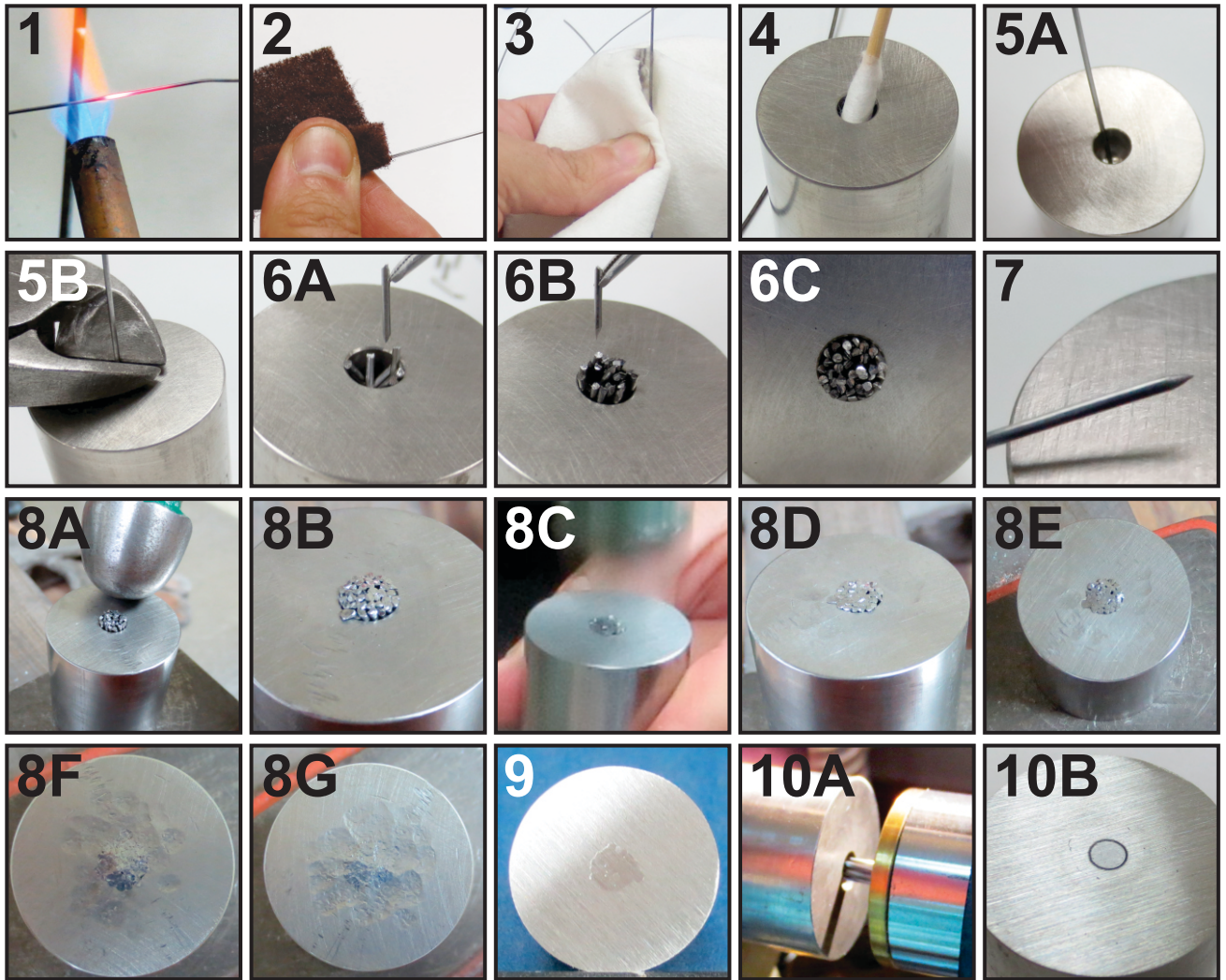
Alignment Tool

The 691-103-974 Clamp Marking Jig Assembly can be used to mark the back of the sample for easy alignment ensuring the sample is directly covering the anode. This can be used for all lamp sizes; 4/14, 2/14, and 2/9. This tool is primarily used for small samples mounted in copper diallyl phthalate. It could also be useful helping when analyzing wires and rods.



Figure 6. Clamp marking jig assembly 691-103-974.

Forging Illustrations



Results of Analysis

Table 2. GDS900 Results of Analysis for Low Alloy Steel Wire Holder Assembly 833-101-139; Forged LAS Wire

Element	Run#1	Run#2	Run#3	Average	STDEV	%RSD
C	0.699	0.700	0.707	0.702	0.004	0.6
Cr	0.087	0.087	0.087	0.087	<0.001	-
Cu	0.113	0.113	0.114	0.114	<0.001	-
Mn	0.866	0.856	0.865	0.862	0.006	0.6
Ni	0.039	0.038	0.039	0.039	0.001	2.3
P	0.013	0.012	0.013	0.013	<0.001	-
S	0.0083	0.0079	0.0088	0.0083	<0.001	-
Si	0.210	0.203	0.210	0.208	0.004	1.9
Fe	98.0	98.0	98.0	98.0		

Table 3. GDS900 Results of Analysis for Low Alloy Steel Wire Holder Assembly 833-101-139; Forged LAS Wire

Element	Run#1	Run#2	Run#3	Average	STDEV	%RSD
C	0.066	0.068	0.066	0.067	0.001	1.4
Cr	0.027	0.033	0.026	0.029	0.004	14
Cu	0.028	0.028	0.028	0.028	<0.001	-
Mn	0.603	0.590	0.593	0.595	0.007	1.2
Ni	0.015	0.018	0.014	0.016	0.002	11
P	0.023	0.022	0.024	0.023	<0.001	-
S	0.013	0.012	0.012	0.012	<0.001	-
Si	0.145	0.141	0.141	0.142	0.003	1.8
Fe	99.1	99.1	99.1	99.1	-	-

Table 4. GDS900 Results of Analysis for Low Alloy Steel (8 mm steel pin) Reusable Wire Holder Assembly 691-103-425; drilled to 8 mm

Element	Run#1	Run#2	Run#3	Average	STDEV	%RSD
C	0.163	0.165	0.164	0.164	0.001	0.7
Cr	0.030	0.028	0.029	0.029	0.001	2.9
Cu	0.017	0.017	0.017	0.017	<0.001	-
Mn	0.942	0.949	0.942	0.944	0.004	0.5
Ni	0.020	0.020	0.020	0.020	<0.001	-
P	0.021	0.021	0.021	0.021	<0.001	-
S	0.014	0.013	0.013	0.013	<0.001	-
Si	0.168	0.169	0.167	0.168	0.001	0.6
Fe	98.6	98.6	98.6	98.6	-	-

Table 5. GDS900 Results of Analysis for Stainless Steel Wire Holder Assembly 833-101-139; Forged 304L Stainless Wire

Element	Run#1	Run#2	Run#3	Average	STDEV	%RSD
C	0.012	0.012	0.011	0.012	<0.001	-
Cr	19.40	19.42	19.43	19.42	0.02	0.1
Ni	9.94	9.90	9.91	9.91	0.02	0.2
Mn	1.719	1.724	1.728	1.724	0.005	0.3
P	0.017	0.017	0.017	0.017	<0.001	-
S	0.012	0.013	0.013	0.012	<0.001	-
Si	0.148	0.148	0.148	0.148	<0.001	-
Mo	0.038	0.036	0.037	0.037	0.001	2.7
Nb	0.006	0.007	0.007	0.006	<0.001	-
Cu	0.063	0.064	0.064	0.064	0.001	0.8
Co	0.057	0.059	0.059	0.059	0.001	1.6
Ti	0.004	0.004	0.004	0.004	<0.001	-
V	0.076	0.075	0.077	0.076	0.001	0.7
Fe	68.5	68.5	68.5	68.5	-	-

Table 6. GDS900 Results of Analysis for Copper Wire Wire Holder Assembly 833-101-139; Forged Brass Wire

Element	Run#1	Run#2	Run#3	Average	STDEV	%RSD
Al	<0.005	<0.005	<0.005	<0.005	-	-
Fe	<0.005	<0.005	<0.005	<0.005	-	-
Mn	<0.005	<0.005	<0.005	<0.005	-	-
Ni	<0.005	<0.005	<0.005	<0.005	-	-
Pb	<0.005	<0.005	<0.005	<0.005	-	-
Sn	<0.005	<0.005	<0.005	<0.005	-	-
Si	<0.005	<0.005	<0.005	<0.005	-	-
P	0.0068	0.0066	0.0071	0.0069	0.0003	3.8
Zn	37.92	38.20	38.08	38.07	0.14	0.4
Cu	62.0	61.7	61.9	61.9	-	-

Table 7. GDS900 Results of Analysis for Aluminum Wire Wire Holder Assembly 833-101-139; Forged Al 2024 Alloy Wire

Element	Run#1	Run#2	Run#3	Average	STDEV	%RSD
Cr	0.024	0.024	0.025	0.024	<0.001	-
Cu	4.67	4.63	4.63	4.64	0.02	0.5
Fe	0.212	0.208	0.204	0.208	0.004	1.8
Mg	1.47	1.44	1.47	1.46	0.02	1.0
Si	0.104	0.103	0.104	0.104	<0.001	-
Mn	0.71	0.70	0.69	0.70	0.01	0.9
Ti	0.015	0.015	0.015	0.015	<0.001	-
Zn	0.081	0.080	0.081	0.080	0.001	0.9
Ni	0.027	0.027	0.030	0.028	0.002	5.6
Sn	0.014	0.013	0.015	0.014	0.001	8.8
V	0.015	0.015	0.016	0.015	<0.001	-
Ca	0.0024	0.0025	0.0025	0.0025	<0.001	-
Al	92.7	92.7	92.7	92.7	-	-

Frequently Ask Questions

Q – How do I determine which lamp is best for my need?

A – This depends on the wire diameter. If wires are <3 mm in diameter, then forging will be required and the standard 4/14 Lamp is the best choice because the finished forged sample is large. If the rod diameter is between 8 and 12 mm, then the 2/9 Lamp is the best choice to eliminate any mounting needed.

Q – Can other shapes be forged besides wires?

A – Yes, we have forged and analyzed ribbon materials.

Q – Are there special concerns we should be aware of before making our decision to go with the smaller anode diameter?

A – The 2/14 Lamp and 2/9 Lamp options have one-fourth the analysis area of the 4/14 Lamp. Results may show a slightly larger standard deviation, however, accuracy is good. These options are often used for irregularly shaped parts that are not candidates for mounting in the holders, for example: screws, small brackets, and ball bearings.

Q – How does the anode and associated o-ring relate to allowable sample size?

A – The sample, as mounted in the holder, seals the system so that proper vacuum can be drawn. The analyzed portion of the sample must be larger than the anode bore so that sputtered atoms only come from the sample. The o-ring must make sufficient contact to hold vacuum at the surface of the mounted sample, so the sample surface must also be larger than the o-ring.

Q – How difficult is it to align the wire sample directly over the anode?

A – It is very easy to align the sample directly over the anode. Since the reamer is aligned with the anode, it also serves as a pointer. Turn on the "Precise Align" option in the Cornerstone Software. Position the sample on the lamp and manually bring in the reamer so that it touches the back of the sample directly opposite the sample. A mark or target may be required. Slide the sample to match the reamer if required. Then press the green switch and close the door.

Close the door as soon as possible; there is a limited time before the sample will drop off. The sample, which is in front, is perfectly aligned with the anode. Upon completion of the analysis, carefully inspect the crater to make sure the entire circumference contains sample and not holder; if it is not, then discard the analysis and make an adjustment to the sample placement on the lamp.

Q – How can I be certain my result has not been contaminated with some of the holder?

A – You can be certain by inspecting the sputter spot (crater). The circumference should be completely in the sample.

Grind the surface again and perform additional analysis. Check the crater after each burn. The holder is made of a stainless steel. Contamination from the holder will show higher Fe, Cr, or Ni results than expected and the standard deviation will suffer.

Q – When is it best to use the standard 4/14 Lamp vs. the 2/9 Lamp?

A – This is based on the amount of surface area available for vacuum seal and analysis. Typically the 4/14 Lamp will work for the majority of wire diameters. The 2/9 Lamp should be evaluated when consistently faced with limited sample surface areas, where the 4/14 Lamp would not meet the sample requirements for the vacuum seal and lamp conductivity.

Q – Why is the standard 4/14 Lamp a better choice for analysis of forged samples?

A – Forged samples are 6.5 mm across—more than ample in size to analyze using the 4/14 Lamp. The 4/14 Lamp is more robust because of its size and achieves better precision due to the increase in the amount of light available to the detectors.

Q – How long does it take to forge a sample?

A – Once a work station is established, the entire process can be completed in as little as 15 minutes. Smaller wire diameters take longer since more sections are required to fill the void in the holder.

Q – How do I remove the sample from the reusable holders?

A – The Sample Holder Assembly 691-103-425 has a set screw that can be loosened to release the wire sample. Gentle tapping may be needed to make the wire fall out. Wire Holder 833-101-139 can be reused by drilling a small hole in the forged wire sample. This will release the force keeping the bundle together.