Wire and Rod Analysis by Glow Discharge

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Instrument: GDS500A

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, 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. Through a process called cathodic sputtering, kinetic energy is transferred from the inert gas ions to the atoms on the sample surface, which causes some of the surface atoms to be ejected into the plasma.

Once the atoms are ejected into the plasma, they are subject to inelastic collisions with energetic electrons or metastable Argon atoms. Energy transferred by such collisions causes the sputtered atoms to become electrically excited. The excited atoms quickly relax to a lower energy state by emitting photons. 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 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 a significant hazardous waste. Glow discharge offers a faster, safer, and 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 follow 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 relatively 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 Performance Note outlines the steps necessary to analyze wire and rods with the GDS500A with various sample holders. The holders provide a means to bundle fine 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 need: Figure 1 shows the three anodes and two o-ring sizes available.

1. The standard lamp with a 4 mm anode can analyze all the various wire sample diameters. Large rods, greater than 15 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 standard lamp can be fitted with an optional 2 mm anode which allows analysis of 3 to 4 mm wires without forging. Only the reamer assembly and anode need be changed, the rest of the lamp parts are common with the standard 4 mm lamp assembly. The o-ring diameter is not changed.
3. The optional small 2 mm lamp, which uses a smaller o-ring, can be used to analyze wires less than 3 mm in diameter wire mounted directly to 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.

Spectroscopy Performance Note

Wire Holder Description

LECO makes available special holders to receive various wire diameters when the size is <12 mm. There are two wire holders available. Sample Holder Assembly 612-708 (Figure 2) comes pre-drilled with a 3 mm pilot hole. It can be drilled to fit larger sized wire or rod (up to 12 mm) and is reusable for that size wire. A set screw on the side tightens the wire in place. An o-ring on the set screw must seal tightly against the holder. Once the individual section of sample is in place a quick dry grind will make sure the sample and holder are both parallel and flat.

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 mm anode and lamp.

Grinding will be required to achieve adequate flatness. Grinding requirements are described in the Sample Preparation section of this note. In time, holders will wear due to grinding of the surface and will require replacement.

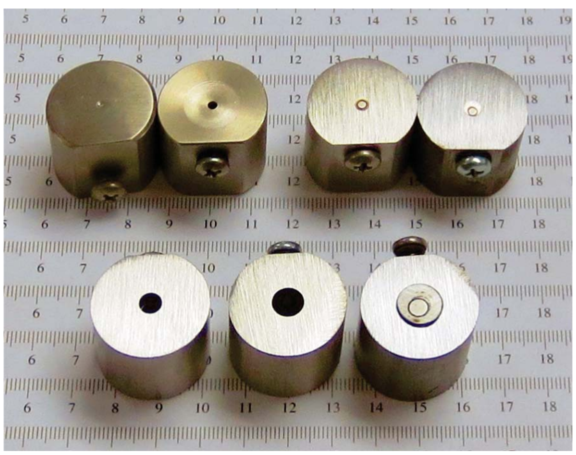


Figure 2. Sample Holder Assembly 612-708.

Figure 3. Wire Holder Assembly 833-101-139.

Figure 2 illustrates the sample holder assembly in various states of use. From left to right in the top row, we see the reamer alignment indent, the standard pilot hole, and two holders with samples of different sizes. On the bottom row from left to right, we see an examples of holders with enlarged pilot holes, and one such holder with an analyzed sample mounted. Figure 3 illustrates the wire holder cavity for forging wires <3 mm in diameter.

Table 1 shows ranges of wire diameters, mounting requirements, and optional lamp/anode sizes. The optional small 2 mm 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		
	Standard Lamp 4 mm Anode	**Standard Lamp 2 mm Anode**	**Small Lamp 2 mm Anode**
≥12 mm	Place Sample Directly on Lamp	Place Sample Directly on Lamp	Place Sample Directly on Lamp
8 mm - 12 mm	Sample Holder Assembly 612-708 required	Sample Holder Assembly 612-708 required	Place Sample Directly on Lamp
5 mm - 8 mm	Sample Holder Assembly 612-708 required	Sample Holder Assembly 612-708 required	Sample Holder Assembly 612-708 required
3 mm - 5 mm	Forging into Wire Holder 833-101-139 required	Sample Holder Assembly 612-708 required	Sample Holder Assembly 612-708 required
≤3 mm	Forging into Wire Holder 833-101-139 required	Forging into Wire Holder 833-101-139 required; 4mm anode can be used	Forging into Wire Holder 833-101-139 required; 4mm anode can be used

Rod Mounting and Analysis

Mounting Directly to the 4 mm Lamp

Rods ≥12 mm can be surface prepped and mounted directly on the 4 mm lamp. Alternatively, these wires can be sectioned bilaterally length-wise providing a large rectangular surface. This method 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.

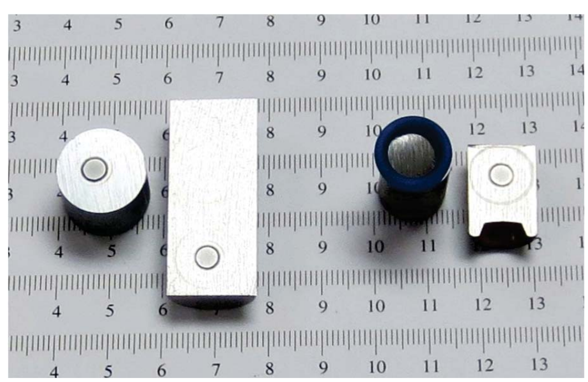


Figure 4. 4 mm Lamp Direct Mount Examples.

Mounting Directly to the Small 2 mm Lamp

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

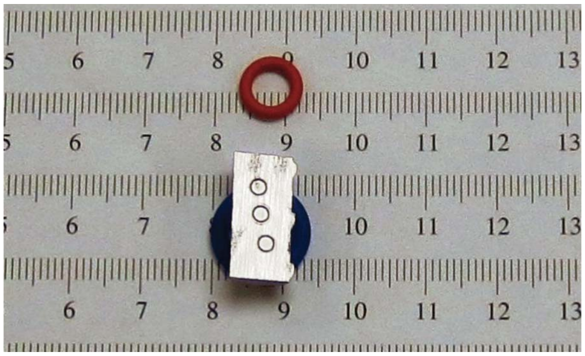


Figure 5. Small 2 mm Lamp Direct Mount Examples.

Using the Sample Holder Assembly 612-708

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 between 10 to 20 mm in length. Place the wire into the holder allowing some to protrude, tighten the set screw and grind the sample flat to the surface of the holder. 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. Sample pockets are present on both sides of the sample holder, so both sides can be used for sampling. 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 a few seconds. Let the wire cool in air. This step can be omitted for already soft materials such as aluminum or copper. Springs can be straightened after annealing.

Sample Preparation

LECO manufactures belt grinders, variable speed polishers, and cut-off saws for metallurgical analysis, these are also suitable for polishing and cutting your sample. 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.

Individual calibrations are required for each 4 mm and 2 mm method. A method calibrated with the 4 mm anode should 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.

Results of Analysis

TABLE 2: RESULTS OF ANALYSIS FOR LOW ALLOY STEEL HOLDER ASSEMBLY 612-708 (Drilled to 6.5 mm dia.)

ELEMENT	RUN#1	RUN#2	RUN#3	AVG	STDEV	RSD
C %	0.38	0.38	0.38	0.38	0.001	0.15
Mn %	1.22	1.22	1.22	1.22	0.001	0.047
Si %	0.23	0.22	0.22	0.22	0.002	0.68
S %	0.017	0.018	0.015	0.017	0.002	8.94
P %	0.022	0.020	0.022	0.021	0.001	5.49
Cu %	0.068	0.066	0.065	0.066	0.001	2.14
Cr %	0.007	0.007	0.007	0.007	0.0001	1.73
Ni %	0.014	0.015	0.014	0.014	0.0002	1.07
Fe %	98.04	98.05	98.05	98.05	—	—

TABLE 3: RESULTS OF ANALYSIS LOW ALLOY STEEL WIRE HOLDER 833-101-139 (Forged 0.9mm dia. wire)

ELEMENT	RUN#1	RUN#2	RUN#3	AVG	STDEV	RSD
Al %	0.015	0.014	0.015	0.015	0.0003	1.88
C %	0.82	0.82	0.82	0.82	0.001	0.14
Cr %	0.044	0.042	0.043	0.043	0.001	2.33
Cu %	0.063	0.063	0.064	0.063	0.001	0.91
Mn %	0.81	0.81	0.80	0.81	0.006	0.72
Ni %	0.022	0.021	0.021	0.021	0.001	2.71
P %	0.021	0.020	0.021	0.021	0.001	2.79
Si %	0.16	0.17	0.17	0.17	0.006	3.46
S %	0.014	0.013	0.014	0.014	0.001	4.22
Fe %	98.03	98.03	98.03	98.03	—	—

TABLE 4: RESULTS OF ANALYSIS ALUMINUM ALLOY WIRE HOLDER 833-101-139 (wire)

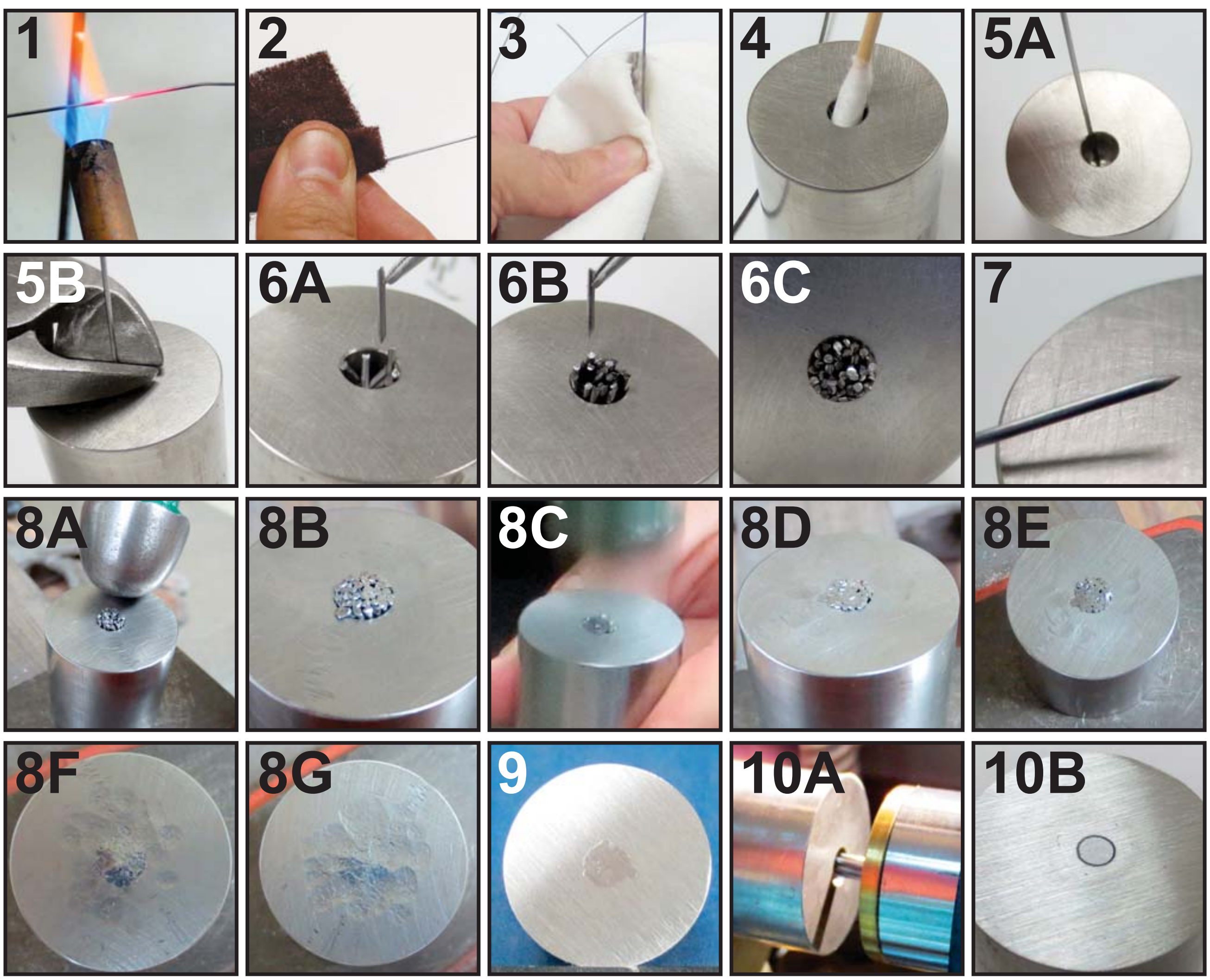
ELEMENT	RUN#1	RUN#2	RUN#3	AVG	STDEV	RSD
Si %	0.11	0.11	0.11	0.11	0.002	2.07
Fe %	0.35	0.33	0.33	0.34	0.013	3.90
Cu %	3.90	3.89	3.90	3.90	0.006	0.15
Mn %	0.61	0.62	0.61	0.61	0.004	0.66
Mg %	1.41	1.48	1.50	1.46	0.047	3.23
Cr %	0.019	0.020	0.020	0.020	0.0001	0.51
Zn %	0.096	0.092	0.099	0.096	0.004	3.67
Ti %	0.022	0.020	0.020	0.021	0.001	5.59
Al %	93.47	93.44	93.41	93.44	—	—

TABLE 5: RESULTS OF ANALYSIS FOR STAINLESS STEEL WIRE HOLDER 833-101-139 (ribbon)

ELEMENT	RUN#1	RUN#2	RUN#3	AVG	STDEV	RSD
C %	0.048	0.047	0.046	0.047	0.001	2.61
Mn %	0.29	0.29	0.29	0.29	0.002	0.80
Si %	0.26	0.26	0.26	0.26	0.001	0.50
Cr %	14.49	14.46	14.41	14.45	0.040	0.28
Ni %	25.01	25.13	25.12	25.09	0.067	0.27
P %	0.022	0.022	0.021	0.022	0.001	2.53
S %	<0.003	<0.003	<0.003	<0.003	—	—
Al %	0.26	0.27	0.26	0.27	0.003	1.05
Mo %	1.16	1.16	1.16	1.16	0.001	0.10
Ti %	2.11	2.11	2.12	2.11	0.004	0.19
V %	0.24	0.24	0.24	0.24	0.002	0.86
Fe %	56.10	56.01	56.07	56.06	—	—

Forging Steps and Illustrations

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 contaminates. (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.



FAQs

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 mm lamp is the best choice because the finished forged sample is large. If your rod diameter is between 8 and 12 mm, then the small 2 mm lamp is your 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 mm anode and small 2 mm lamp options have one-fourth the analysis area of the 4 mm lamp. Results may show a slightly larger standard deviation, however, accuracy is good. The 2 mm option is more 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 serve as a pointer. Place the sample against the o-ring and manually push the reamer against the back of the sample so that it touches the center, then slide the sample to match the reamer if required. 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 your centering technique.

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

Q – Why is the standard 4 mm 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 mm lamp. The 4 mm 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 612-708 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.

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