Preparation of Specimens for Bulk Analysis Using LECO Glow Discharge Spectrometers

Introduction

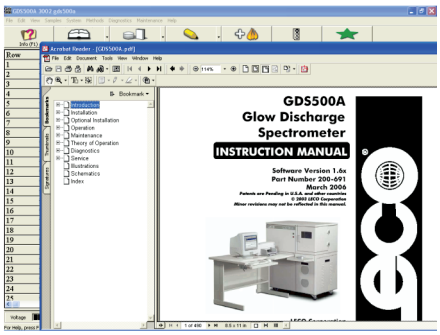
Information in this document pertains to all LECO Glow Discharge Spectrometers, including the GDS850A and the GDS500A. The purpose of this material is to provide recommendations and associated procedures for different sample preparations prior to presenting the sample to the GDS system. Whether your sample is a block, powder or wire, there is a way to obtain an analysis using GDS, and a variety of sample preparation techniques are included here.

Safety Practice

This document does not assume to address all of the safety concerns, if any, associated with its use. It is assumed that all who use these procedures will be trained analysts capable of performing common laboratory procedures skillfully and safely. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. The use of the appropriate equipment such as safety glasses, dust masks, and gloves shall be employed as necessary.

Electronic Manual

The electronic manuals included with all LECO Glow Discharge Spectrometers are an excellent source of information. They utilize diagrams, software illustrations, and photographs to guide the user through daily operation and infrequent tasks such as routine maintenance. To use, simply open the info-folder icon or "Help" pull-down and perform a search on the topic of interest. "Sample preparation" is a good example. The GDS500A help file states, "The sample surface must be flat to obtain the proper vacuum seal…". A table describing recommended surface preparation media is also available in the help file.



The Importance of the Sample

The sample is part of the lamp during analysis and therefore plays a role in the correct functioning of the lamp. The sample becomes part of the cathode potential. It serves two purposes—completes the electrical circuit and seals the vacuum chamber. In order for the plasma to form and sputtering to occur, the sample must touch the cathode, and must seal sufficiently tight to pull vacuum. When analyzing mounted samples, the mount electrically bridges and seals the lamp. Adequate sample flatness is achieved by any common mechanical means such as a belt grinder or wheel polisher. When placing a sample on the lamp, press it firmly against the blue o-ring. The operator then pushes a switch to actuate the vacuum thereby holding the sample in place (up to a half-pound sample weight). A sample that is not flat may not seal properly, resulting in a poor vacuum and an improper or failed analysis. Porous samples, pits, or gas holes and overlapping of a previous sputter spot may also cause poor results.

Avoid touching the analytical surface of the sample and the lamp. Wipe the anode with the foam wiper after the reaming cycle or just before mounting the next sample.

Spectroscopy Performance Note

Delivering the Right Results

Maximum Sample Size That Can be Accommodated

The LECO GDS can accommodate generous sample sizes. The GDS500A chamber can accommodate samples up to 400 mm deep (X) by 300 mm tall (Y) by 40 mm thick (Z). The GDS850A can accommodate samples up to 200 mm deep (X) by 250 mm tall (Y) by 50 mm thick (Z). Samples larger than these dimensions will need to be sectioned to fit in the chamber and on the lamp. The distance between the lamp and the reamer bit is the smallest dimension and most probable reason to section samples. For heavy samples the GDS500A features manual actuation of the reamer to serve as a holding mechanism. A "lab jack" or other non-conductive block may also be used to help keep the sample in place.

Typical Samples and Size Requirements

The most regularly shaped samples that are seen in the laboratory are in the form of chilled disks 40 to 50 mm in diameter. Disks are more than sufficient in size to be analyzed and can be homogenous if made correctly. Disks should be analyzed to the outside, close to the edge where rapid cooling has taken place. The top pour spout and bottom should be avoided. The correct amount of "skin" should be removed from the analytical face per ASTM guidelines; for example refer to ASTM Method E716-85EN for aluminum disks.

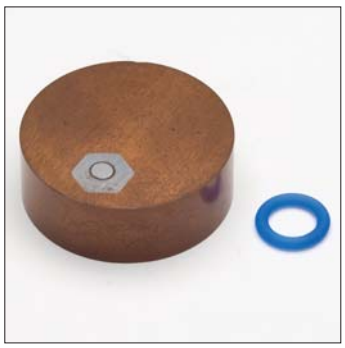
Irregularly shaped samples may be analyzed directly without any special treatment other than surface abrading. Wrenches, sockets, nuts, and rods have been analyzed by grinding a flat surface onto the sample and placing it on the lamp.

In cases where the back of the sample is oddly shaped, such as having a slope, it may be necessary to grind a flat or place a block between the sample and reamer bit.

Minimum Sample Size That Can be Analyzed

The table below illustrates the minimum sample sizes that can be analyzed without any additional preparation other than surface abrading.

Lamp	Anode	O-ring	Sample
Standard	4 mm	15 mm	>15 mm x 15 mm
Standard	2 mm	15 mm	>15 mm x 15 mm
Small	2 mm	9 mm	>9 mm x 9 mm



Preparation techniques that allow for analysis of extremely small sample types such as wires <1 mm in diameter and powder samples <320 mesh have been developed. The sample must be made larger by one of the techniques discussed below. The minimum final size of the sample must be 4.5 mm (4 mm anode) and 3 mm (2 mm anode).

A Quick Gauge to Check Sample Size

Carefully remove the o-ring from the lamp face and place it on your sample. Is the analytical surface of the sample large enough to seal completely around the o-ring and touch the lamp face? If the answer is "yes", then you are ready for sample preparation and analysis. Refer to the help file for recommended finishes; search for "preparation".

Small Sample Types <15 mm

If the answer to the question above is "no", then more preparation is needed before continuing. There are several possible solutions.

- It may be possible to section the sample in such a way as to give a larger surface; refer to the paragraph on "sectioning".
- Samples that seal on the o-ring but do not quite make contact with the lamp face are candidates for pressing; refer to paragraph on "pressing samples".
- Samples smaller than the blue o-ring but larger than the anode should be mounted in copper diallyl phthalate; refer to "mounting in copper diallyl phthalate".

- Samples about the same size or smaller than the anode are still possible. Try pressing the sample to get it a bit larger, and then mount in copper diallyl phthalate.

Small samples are subject to more heat from the analysis, they have less mass and limited contact with the water cooled lamp. A block of scrap material can be placed between the reamer and the sample to transfer heat from the sample. Poor results may be obtained if the sample becomes overheated.

Sectioning

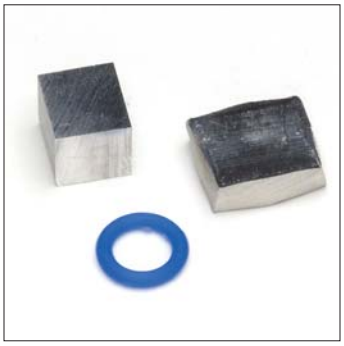
LECO manufactures a complete line of metallographic equipment including sectioning saws. The saws offer useful options such as an X-Y table for exact positioning of specimens for excision. To conserve sample, use the thinnest blade as practical. Evaluate the sample carefully and section to reveal the largest surface area for analysis; even if the sample is to be mounted, the goal is to end with the largest sample as possible. A large sample is easier to locate on the lamp and may have space for multiple analyses around the piece without grinding to reveal a fresh surface. For example, in a "+" headed screw, the section should be made behind the head, cutting off the screw shaft. The head of the screw opposite the "+" is the largest flat area of the sample.

Mounting in Copper Diallyl Phthalate

Small samples <15 mm should be mounted in an electrically conductive media such as copper-filled diallyl phthalate thermosetting resin. When mounted, the media makes electrical contact with the sample and the cathode plate. The copper mount also helps with keeping the sample cool. Samples may need to be sectioned to fit inside the cavity of a metallographic mounting press such as the LECO PR-32. Section the sample to be as large as possible for easier alignment on the lamp. Thickness should be no more than ¼ inch if possible; thicker samples will require more mounting media. Sharp square edges should be abraded down since they may cause the mount to crack. A flat can be ground onto the surface to be analyzed so that it lies against the platen of the press. This will reduce the amount of surface grinding later.

The entire mount can be made of the copper diallyl phthalate (PN 811-139); however, we find that using approximately 10 g to cover the sample is sufficient when backed by 5 g of the less expensive blue diallyl phthalate thermosetting powder (PN 811-135). The blue media does not soften with heat and resists the force of the reamer. Use a caliper to measure the coordinates of the sample and mark the back of the mount exactly opposite to the sample. When placing the sample on the lamp, align the reamer bit to the mark placed on the back. This will perfectly align the analytical portion of the sample with the anode.

Pressing Samples



This technique slightly expands the size of a sample, making it possible to be analyzed either directly or by first mounting. A commercially available hydraulic press capable of pressing to 20 metric tons is adequate. The sample is placed in between two hardened steel platens and pressure is applied. Depending on the analytical area surface, the sample can be analyzed using the 4 mm or 2 mm anode. Use a backing plate for a heat sink during analysis so that the sample does not over heat. Having a flat and abraded back side ensures good thermal contact with the cooling block.

Reusable Holders

LECO manufactures a reusable holder designed to routinely analyze small diameter rod type samples >3 mm (PN 612-708). It requires that the rod be of uniform diameter and sectioned to fit inside the holder. The holder comes with a pilot hole, which is enlarged by the user to exactly match the dimension of the sample. Multiple holders can be fashioned and made available to routinely accommodate a variety of diameters. The outside of the rod sample shall be de-oiled and abraded to remove any surface contamination and oxidation. The sample is placed inside the holder and fastened in place so that the face of the sample is flush with the holder face. A light grind can make sure of sample flatness

and provide a clean face for analysis. The holder is placed on the lamp with the sample directly over the anode. Analysis is then initiated. After analysis the sample is ejected and the holder reused with another sample of the same diameter.

Forging

This procedure is useful for small diameter rods, wires, and springs. Annealing to a dull red may be needed to soften the material. The specimen shall be straight or made to be straight. The sample is abraded and then cut using wire cutters. Next, wash using ethyl acetate to remove any remaining contaminates. The cut pieces are then packed tightly, parallel to each other, into the wire holder (PN 833-101-139). A peening hammer is used to forge the cuttings into place to form a single mass to be analyzed. The sample and block are surface abraded using a 120-grit zirconium oxide belt (PN 810-499) on the LECO BG-30 (PN 802-400-100). The steel block may be reused by drilling a small diameter hole into the sample, which allows the wires to be removed.

Powder Metals

Samples made from powder metal that are less than fully dense can also benefit from pressing. Keep in mind that a large part will cause the force of the press to be spread out over a larger area. Sectioning the sample down to 15 mm x 15 mm x 5 mm will concentrate the PSI. Should the sample break apart when pressure is exerted, another sample should be obtained that is more malleable. Re-melting the sample into a button could be considered as an option.

De-Lubing Powder Metal Samples

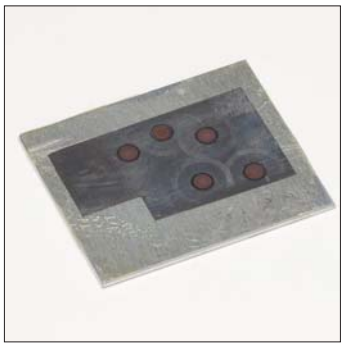
Powder metal samples should not be analyzed "green" as they are not fully dense and may contain organic lubricants and/or binders. Porous oil-filled specimens designed as "lifetime" bearings are also candidates for this procedure. The organic substances must be removed prior to analysis. Heating the sample to 650°C in a muffle furnace such as the LECO TGA in an inert atmosphere (nitrogen or argon) for 1 hour is usually sufficient for most sample types. When heating is done, slowly cool and treat as any normal sample. Powder metal samples that are not fully dense may benefit from pressing in a hydraulic press.

Powders; Metal and Non-Metal (Slags & Limestone)

Powders <320 mesh such as copper, zinc, and aluminum powders have been successfully analyzed. Commercially available pellet dies are available to use with a hydraulic press to produce a sample disk. Limestone and slag powders have also been analyzed by first mixing with pure copper powder. Contact LECO for more information concerning powder analysis.

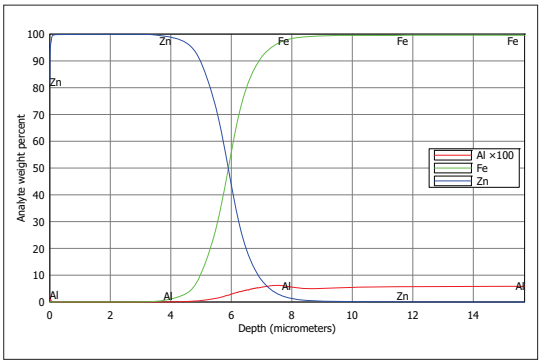
Thin Samples

Thin samples such as sheet metal less than 0.5 mm can be analyzed directly on the GDS by gluing the specimen to a conductive substrate. The substrate provides rigidity and acts as a heat sink to prevent overheating the sample. The bonding surfaces must be clean and free from fingerprints and oily residues. A strong degreaser such as ethyl acetate will accomplish the task. The bonding material is two-part, quick-setting epoxy. Mix in accordance with the manufacturer's instructions. Evenly spread a thin coat on the substrate material and place the thin specimen onto the glue. Protect the analytical surface with a polyethylene sheet, cover the plastic with a spare substrate and gently but firmly clamp the unit during the curing process. Continuously apply the gentle pressure until the epoxy has cured.



Surface Treatments

Bulk analysis of the substrate will yield the most representative results. Some samples may have a coating or heat treatment that changes the specimen chemistry to a certain depth. Bulk analysis using Glow Discharge cannot by itself determine if there is a surface treatment present. To ensure the analysis of virgin material, the outside case or coating shall be completely removed. Alternatively the sample can be sectioned and analyzed on the "inside", away from any surface treatment or contamination.



Compositional Depth Profile requires QDP software on the LECO GDS850A. Coatings such as Zinc-Galvanized, PVD, CVD, Plating, and Cladding can be analyzed in minutes. Please be sure to look at the specific application notes regarding CDP analysis at **www.leco.com** (resources/applications library/spectroscopy).

Conclusion/Synopsis

It is evident that Glow Discharge Atomic Emission Spectrometry can analyze many types of sample morphology. In fact, GDS holds the advantage over alternative techniques when it comes to analysis of small or thin samples. LECO is committed to helping you get the right result through applications development of varied sample types.

- An excellent instrument manual is supplied with the GDS systems.
- Large samples can be sectioned to fit on the glow discharge lamp.
- Samples can be sectioned to reveal the largest face (area) for presentation to the lamp.
- The sample must be flat and form a vacuum seal against the blue o-ring.
- The sample must completely cover the o-ring and contact the face of the lamp (>15 mm) for electrical conductivity.
- A marginally sized sample can be made larger when flattened using a hydraulic press.
- Samples <15 mm must be mounted in copper dialyll phthalate for completing the vacuum seal and electrical conductivity.
- Samples >4.5 mm in diameter can be analyzed using the 4 mm anode.
- Samples as small as 3 mm to 4.5 mm and larger in diameter can be analyzed using the 2 mm anode.
- Re-usable rod and wire holders are available for routine analysis.
- Wire samples smaller than 3 mm can be forged and analyzed using the 2 mm or 4 mm anode.
- Powder metal samples can be routinely analyzed if fully dense and contain no lubrication.
- Powders can be analyzed when pressed into a disk.
- Thin specimens can be glued to a rigid substrate using two-part epoxy.
- All samples should be finished in accordance with the final preparation chart in the instruction manual.
- Grinding or abrading the sample to remove coatings or treatments is required in order to achieve accurate analytical results of the specimen substrate.
- Surface analysis is possible using the QDP software available with the GDS850A.
- LECO will assist with your specific application needs through a dedicated GDS spectroscopy service team and the Solids Spectroscopy Applications Laboratory.

LECO Corporation
3000 Lakeview Avenue • St. Joseph, MI 49085 • Phone: 800-292-6141 • Fax: 269-982-8977
info@leco.com • www.leco.com • ISO-9001:2008 HQ-Q-994 • ***LECO is a registered trademark of LECO Corporation.***

Form No. 209-076-031 *11/12—REV1*

Spectroscopy Performance Note