Analysis of Galvanized Steel Plates Using Glow Discharge-Atomic Emission Spectrometry

Liang Wang
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ANALYSIS OF GALVANIZED STEEL PLATES USING
GLOW DISCHARGE-ATOMIC EMISSION SPECTROMETRY

A Thesis Presented to
the Faculty of the Department of Chemistry
Western Kentucky University
Bowling Green, Kentucky

In Partial Fulfillment
of the Requirement for the Degree
Master of Science

by
Liang Wang
August, 1999
ANALYSIS OF GALVANIZED STEEL PLATES USING
GLOW DISCHARGE-ATOMIC EMISSION SPECTROMETRY

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Liang Wang
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ANALYSIS OF GALVANIZED STEEL PLATES USING
GLOW DISCHARGE-ATOMIC EMISSION SPECTROMETRY

Liang Wang  
August, 1999  65 Pages

Directed by: John T. Riley, Wei-Ping Pan, Charles Lee

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Combining an intense emission source and a high-speed sputtering source in one, glow discharge atomic emission spectrometer (GD-AES) provides an efficient technique for analyzing surfaces, coatings and bulk solids. The purpose of our work is to explore the optimum lamp operation parameters of SA-2000 for analysis of galvanized steel plate and to investigate the method for qualitatively and quantitatively analyzing the zinc coating. Under the optimum experimental conditions found in our study, which are current of 19-21 mA; voltage of 900-1200 V; pressure 2.0-2.5 torr, the calibration curve is constructed, so that specific zinc concentration can be assign to the exact depth position in the sample. Several galvanized steel plate samples are tested and the thickness of coating and distribution of zinc in different depth of the coating are calculated on the basis of calibration curve. The above results are further analyzed to prove the reproducibility of the proposed method.
I. INTRODUCTION

A. History of Glow Discharge Devices

With the developments and advances in materials research, more and more challenges are being imposed in analytical chemistry. One such challenge is the direct analysis of solid materials, such as solid surfaces, layer coatings and bulk substrates. Direct analysis of these samples is always a prime objective for industrial atomic spectrometry. In order to successfully accomplish the elemental analysis of solids, the employed spectrochemical source is anticipated to be (1) applicable to all possible sample matrices (bulk and particulate, electrically conductive and nonconductive), (2) easy to control the atomization/excitation/ionization rate, (3) rapid for high-precision profiling, (4) convenient to use, and (5) able to operate in a multimode (e.g., AA, AE, MS). The glow discharge (GD) source is considered an important device in the area of direct solids elemental analysis because of its capability to fulfill the above requirements.

Glow discharge generally refers to low power electrical discharges in reduced pressure systems. A GD device is capable of generating a representative atomic population of a solid sample and producing both excited state and ionic population of atoms. A large variety of light sources can be classified as glow discharge devices, and some of them are involved in our daily life — such as neon lights and the ordinary fluorescent tube.
Glow discharge devices have a rich history of applications dating back to the early decades of this century. Since they were first introduced in 1912 in fundamental spectroscopic studies of atomic structure, GD devices have developed and improved slowly but steadily, especially after the commercial glow discharge spectrometry (GDS) instruments became available in late 1970s. The primary uses of glow discharge devices in the fields of analytical chemistry are as line sources in atomic absorption spectrometry and in bulk solids elemental analysis by atomic absorption, emission and mass spectrometers. More recently, they have been applied in laser-enhanced ionization and resonance ionization mass spectrometry. Now GD devices are also widely utilized in the production of electronic devices and components in metal vapor lasers. It should be realized that the applications of GD devices will be extended even further with the improvements in their designs and performances in the future.

B. Theory of Glow Discharge Devices

Glow discharge devices are reduced-pressure, inert-atmosphere, and gaseous conductors. In a glow discharge lamp two parallel plates, one the cathode and the other the anode, are separated by several centimeters in a glass vacuum chamber. The cathode is usually made or fabricated from the investigated sample. A glow discharge, initiated as the support gas, is introduced into the chamber and a sufficient voltage is applied across the electrodes. The discharge gas could be any type of gas in practice, but noble gases are commonly used, in order to avoid chemical reactions during operation. To initiate the discharge, the applied voltage must exceed the energy necessary to break down the discharge gas, and this minimum value is a function of the geometrical design, electrode material, discharge gas and pressure. In a noble gas atmosphere at a pressure of
approximately 0.1 to 10 torr, the supplied voltage is usually 500 to 2000 V to initiate a discharge.

This high voltage across the electrodes will result in the breakdown of the discharge gas (typically argon gas), so that the positively charged ions as well as free electrons are generated. The positively charged argon ions are accelerated to the cathode surface as a result of the electric field gradient established from the relative potential on the electrodes. The moving of the charged ions or electrons will lead to a current, and the charged ions will transfer their energy to the atoms of the cathode surface. Consequently, sputtering clusters of cathode material, ionic species, and secondary electrons are set off. The process of catholic sputtering is the means of sample atomization and the basis for depth-resolved analysis. This phenomenon of current flowing through a gaseous medium is termed a "discharge."

After the initial breakdown of the discharge gas, collision within the discharge aids in producing more ions or electrons. The secondary electrons play an important role here. Collisions with the secondary electrons will ionize the sputtered material and discharge gaseous atoms into the gas phase to sustain the discharge. At this point the discharge is said to be "self-sustaining" provided that a suitable voltage, which is usually significantly lower than the breakdown voltage, is continually applied. The maintaining voltage is dependent on the discharge current, fill gas identity and its pressure in the source, cathode identity, and the particular electrode configuration. 

A normal glow discharge plasma can be physically divided into three prominent sections: the cathode dark space, the negative glow, and the Faraday dark space. In the vicinity of the cathode, the electrons lose most of their kinetic energy through collision with gas atoms, and the drop of the entire potential between the two electrodes occurs
here. It is known as the cathode dark space because of its noticeably low luminosity. Beyond this region is a bright band, which is called negative glow, located a few millimeters away from the cathode. In this region, there are plenty of electrons with sufficient energy to cause excitation. Argon atoms are excited in this region into their metastable states and then collide with sputtered atoms to cause them to be excited. These excited states of sputtered atoms are rather unstable and the electron configuration soon returns to its ground state with the emission of photons with characteristic wavelengths, resulting in the emission. This process is the so-called de-excitation or relaxation. Most analytical information is acquired in this region. Sometimes the glow discharge plasma may exhibit Faraday dark space, positive column, anode dark space and anode glow regions. However, when the anode is brought closer to the cathode, the positive column disappears and the dominant features remaining are the cathode dark space and the negative glow, since these two portions offer plenty of analytical information.

The photons with characteristic wavelengths emitted in the negative glow region are then detected by optics to examine the material being sputtered from the cathode. This emission and detection process is the basic principle of glow discharge atomic emission spectrometry (GD-AES). The photons, whose wavelengths range from 100 nm to 800 nm, pass through a window on the lamp and then into at least one optical spectrometer. The spectrometer can be either a polychromator or a spectrophotometer with many fixed channels each set to a different wavelength for recording many elemental signals simultaneously, or a monochromator, i.e., a spectrophotometer with one channel whose spectrometer is tuneable over a wide wavelength range.
C. Two Power Mode (dc and rf) GD Sources

There are two different modes for operating GD sources. If the voltage applied across the electrodes is constant (dc), then conductive materials can be analyzed. If the voltage is radio frequency (rf) alternated, then both conductive and non-conductive materials can be analyzed.

1. dc GD Source

The most commonly used dc GD source is a Grimm type lamp, which is based on the design developed by Grimm in 1968.\(^7\) The development of the Grimm type lamp led to a primary step towards the development of the commercial GD-AES analyzer. The principle of the Grimm type lamp is illustrated in Figure 1. In essence, the lamp is comprised of a tiny vacuum chamber consisting of a hollow brass tube as the anode and the sample as the cathode. Usually, a window which is made from MgF\(_2\), or similar material, is installed in the Grimm type lamp in order to transmit photons in the wavelength range of 100-800 nm.\(^4\) The sample is mounted onto an o-ring seal made from a relatively soft material, completing the vacuum chamber. In normal operation, little specimen preparation is required.\(^4\) Quite large samples, particularly in dc operation, can be handled, perhaps as large as 200 mm across. Special mounts are available for wires and rods. The sample surface should be sufficiently flat to seal the o-ring. Besides those materials with the correct shape, the Grimm type lamp is also applicable to the solid samples in powder form, since the sample powder can be mixed with copper or graphite powder and pressed into pellets. A procedure for preparing copper pellets was described by Winchester and Marcus.\(^8\) A specific procedure for combustion residues slags limestone, and ceramics was developed in the Coal and Fuel Laboratory at Western Kentucky University. Ash particles were mixed with copper powder, pressed into pellets
Figure 1. A schematic of the Grimm type lamp used in a glow discharge atomic emission spectrometer.
and then subjected to the GD-AES analysis, in order to obtain the information about the
major and trace elements present in the ash.  

The Grimm type lamp body is normally kept at ground potential, and the water-
cooled, isolated front plate is at negative potential during operation. The tube-shaped
anode fits tightly into the central opening of the front plate. During operation, the
chamber in the Grimm lamp is evacuated, normally by rotary pumps. Consequently, the
atmospheric pressure outside the sample compresses the o-ring to seal the sample on the
front plate. The annular face of the anode is located only 0.1-0.2 mm away from the
surface of the sample. The distance between the anode and sample is smaller than the
dark space so that no discharge is possible there; thus all of the sputtering of the sample
surface takes place in the region opposite the hollow of the anode. Argon is bled
continuously through the anode and out to the vacuum pumps. The sample surface is
continuously eroded by bombardment of ions and neutrals from the plasma (cathodic
sputtering), and sputtered sample atoms diffuse into the plasma before being adsorbed on
a cold surface inside the source. A substantial fraction of the sputtered atoms are
deposited on the sample surface, and a dynamic equilibrium is established at an “effective
sputtering rate,” sometimes referred to as the sample loss rate. While in the plasma, some
sample atoms are excited and emit element-characteristic atomic emissions. A fraction of
atoms will also be ionized allowing detection by mass spectrometry.

The argon pressure inside the lamp during sputtering is typically 2-10 torr. The
applied voltage varies between 400-1200 V for a dc source. When the current-voltage-
pressure conditions are right inside the lamp then very flat and very fast sputtering of the
sample occurs. The homogeneous electric field distribution in the active region ensures
that the sample surface is sputtered rather evenly, resulting in a crater with a nearly flat
bottom. By recording the analytical signals (intensity of optical emission) as a function of sputtering time, an elemental depth profile is obtained.

Although the Grimm type lamp was originally intended as an alternative to the spark source for routine bulk analysis,\textsuperscript{10,11} the Grimm GD has proven to be an ideal tool for depth profile analysis. Greene and Whelan in 1973 in the United States\textsuperscript{12} and a little later Berneron in France\textsuperscript{13} realized the feasibility of the Grimm Lamp for rapid depth profiling. In 1972, Boumans showed how sputtering rates could be related to the lamp parameters of current, voltage and pressure.\textsuperscript{14} In the 1980’s the first quantitative methods for depth-profiling were developed.\textsuperscript{15} The position of the Grimm type lamp to serve as a major source for the depth profiling analysis was established thereafter.

2. rf GD Sources

Until the late 1980’s, only dc power was used as a GD device, in which a constant voltage was applied to the electrodes. This technique created a niche in the sheet metal industry and in automobile manufacturing, especially in zinc-iron and zinc-nickel coated steels.\textsuperscript{16-19} However, dc operation restricted the GD-AES technique to conductive materials only, thus the industrial application of GD-AES was limited to the metals and metallic coatings. The capacity of the instrument was extended dramatically in 1988, when Chevrier and Passetemps in France and later Marcus in the United States\textsuperscript{20} applied a radio frequency (rf) voltage to the sample. With rf power, GD-AES is able to analyze and depth-profile both conductive and non-conductive substances, including metals, polymers, ceramics, glasses, and biological samples. This capability is of paramount importance for surface and depth profile analysis, since there exist numerous technically and industrially important non-conductive materials, such as paints, that are extremely
difficult to analyze by any other techniques. However, the procedures have to be developed empirically.

The first commercially available rf GD sources were based on the Grimm design concept, allowing both dc and rf operation by simply interchanging some parts of the source. Marcus also designed a GD source that is only suitable for the rf power mode. Besides the rf-only mode of operation, this source differs physically from the Grimm type primarily in eliminating the isolated front plate, the hollow anode being an integral part of the front end.

In most studies involving rf power, the rf frequency employed in GDS is 13.56 MHz. This rf voltage is applied directly to the sample, which acts as one electrode (the cathode), while the other electrode (the anode) is held at ground potential. Argon gas is bled between the two electrodes. Free electrons between the sample and anode are driven backwards and forwards at high speed by the rf field. These electrons will ionize the argon gas. Since the argon ions have much greater mass, they are unable to respond as rapidly as the electrons to the fluctuating field, so that the electrons and ions therefore can become separated in space. The electrode with the smaller surface area, in this case the sample (cathode), will have a stronger field than the larger electrode (anode). As a consequence the sample will quickly become negatively biased. The negative bias of the sample is approximately half the applied rf voltage. This self-bias is equivalent to a dc voltage applied between the sample and the anode. The more slowly moving, positively charged argon ions will thus be driven by the self-bias into the sample, causing sputtering of the sample surface.

According to the paper by Duckworth and Marcus, the analyte ion currents observed in the dc and rf power modes are similar when glow discharge plasma was
utilized as the ionization source for mass spectrometry. More recently, Payling and coworkers reported a comparative investigation on quantitative analysis of surface layers coated on steel substrates with a Grimm type glow light source operated in either dc or rf modes. It was found that the two modes have similar analytical parameters such as the calibration factors and the background equivalent concentrations.

Prassler and co-workers investigated the correlation between depth resolution and the crater formation process for depth profiling in two glow discharge modes (dc and rf). By using conductive samples with a well known multilayer structure, the discharge parameters for maximum depth resolution were determined and crater formation during the sputtering process was examined. It was found that the best depth resolution was at the same values of pressure and power for both modes.

In the study conducted by Kazuaki Wagatsuma, they investigated the intensity variations of Ar(II) emission lines, which are identified in different transitions when a Grimm glow discharge source is operated with either dc or rf power supplies, and measured the emission intensities of an analyte and the sputtering rate in both power modes as well, in order to compare each plasma condition. They confirmed that the emission characteristics of the dc and the rf powered Grimm glow discharge plasmas are rather similar, when using the argon spectral lines to examine the plasmas. The result agrees with previous work and thus implies that equivalent conditions for emission of the analyte could be determined for both power modes.

D. Quantitative Depth Profile (QDP) Analysis with GD-AES

Quantitative depth profile (QDP) analysis is an important application of the GD-AES technique. Most conventional approaches using glow discharge sources are
frequently applied to the determination of elemental depth profiles. GD-AES effectively combines a high-speed sputtering source and an intense emission source in one, so as to provide a modern, extremely rapid technique for analyzing surfaces, coatings, interfaces, and bulk solids. With direct current (dc) and radio frequency (rf) modes currently available, GD-AES is widely used to analyze industrial materials, to determine the composition of layers at the extreme surface, the distributions of elements in metallic and polymer coatings, and the composition of metal alloys, polymers, and glasses.

1. Calibration

Calibration is an essential step in depth-profile analysis. In analyzing a sample with GD-AES, the primary data obtained is in the form of intensities of the characteristic lines for individual elements as a function of sputtering time. This information is normally presented in diagrams, which in a qualitative way represent elemental depth profiles through the corresponding surface layers. The intensities of elemental emissions as a function of time should be converted into elemental concentration as a function of depth below the surface of the sample. Such conversion process is called performing a quantitative depth profile (QDP).

Similar to most types of spectrochemical analysis techniques, solution for quantification problems in GD-AES has to rely on the use of standards, or calibration samples of well-known chemical composition. Standards can be either in the form of homogeneous bulk materials or substrates with a well characterized surface coating.

The standard AES methods for accurate quantification of the elemental concentrations of bulk materials are well established. However these approaches are not generally applicable in depth profile analysis, since matrix effects which influence and
complicate the determination of concentration and sputter rate must be taken into account in QDP. In contrast to bulk analysis, in which the homogeneous samples of a rather well-known matrix composition are measured, the depth profile analysis usually involves a multi-matrix system. In bulk analysis, calibration of the analytical system is carried out with a set of calibration samples of compositions similar to the unknown samples. However, the different layers encountered in a depth profile often represent widely different material types (matrices). Another complication for the calibration procedure concerns the electrical parameters, since the parameters for the source (voltage, current) often vary considerably as layers of different composition are penetrated. Such variations may notably influence the signal intensity, and must be considered in a complete quantification method.

Several methods and empirical equations have been adopted to mathematically relate the sputtering time to the sputtered depth and emission intensities to elemental concentrations as well. The possibilities for using standard bulk reference samples, which are readily available at reasonable cost, are realized through these assumptions and equations.

Under most circumstances in dc GD-AES (the calibration for rf GD source is discussed in the Further Study section), the relation between emission intensity and elemental concentration can be expressed as follows:

\[ I_{a,s} = Y_a \times C_{a,s} \times S_s + B_s \]  \(1 \)

\( I_{a,s} \) = Emission intensity from analyte \( a \) in standard \( s \).

\( Y_a \) = Emission yield of analyte \( a \). It is defined as the number of photons emitted per supplied atom. The emission yield is independent of the matrix.

\( C_{a,s} \) = Concentration of analyte \( a \) in standard \( s \).
S_s = Sputtering rate of standard s.

B_s = Matrix independent background of analyte a.

The above equation is established on the following assumptions:

a. The sputtering and excitation of the sputtered particles in the argon plasma are deemed independent.

b. Emission yield and background for each analyte do not depend on the sample composition, and they only depend on which element is to be detected.

c. Sputtering rate depends only on the matrix.

In the above model, any preferential sputtering is ignored and it is assumed that all elements are sputtered from a given sample at the same rate. These assumptions have been investigated by several researchers and are widely recognized to be valid.

Normally, the emission yield is a function of voltage and current. Bengtson at the Swedish Institute for Metal Research (SIMR) advanced an empirical equation for emission yield.\(^6\)

\[
Y_a = i_g^{A_m}(V_g - V')^{B_m}
\]  

Where \(i_g\) and \(V_g\) are the current and voltage, respectively.

\(V'\) is the threshold voltage.

\(A_m\) and \(B_m\) are constants.

In principle, calibration for quantitative depth profile is carried out by measuring a set of bulk calibration samples. It is normally necessary to use samples of different material types, including a number of pure elemental standards. The samples, which should be selected to cover all elements of interest in appropriate concentration ranges, are all analyzed at the same excitation condition. As the sputtering rates of these calibration samples vary with the different matrices, the measured intensities will
normally show considerable scatter. For the purpose of compensating for this effect, the concentration should be corrected to the sputtering-rate corrected concentration thereafter, which is implemented by simply multiplying the sputtering rate of each calibration sample by its concentration. This correcting step is shown in Figure 2. Therefore, besides the concentration, it is necessary to know the sputter rate of the calibration samples.

The calibration curves are constructed, in which the intensity of a characteristic emission line is illustrated as a function of the corrected concentration (the product of the concentration of element in sample and the sputtering rate of this sample). When an unknown sample is examined, the measured emission intensity can directly correspond to the corrected concentration from the calibration curve. However, neither of two parameters needed to calculate the corrected concentration is known. Deduced from the calibration plot, the unknown concentration can be expressed by

\[ C_x = \frac{(I_x - B_x)}{Y_x} \cdot S \]  

Where \( I_x \) is the intensity of the element of interest, which is determined by GD-AES.

\( B_x \) is background for the element of interest, which is independent of the matrix. It is the intercept on the calibration curve.

\( Y_x \) is the emission yield of the element of interest, which is the slope of the calibration curve and independent of the matrix as well.

It is reasonable to assume the sputtering rate as a constant during a very short period. Because the sum of the concentration for all elements in the sample equals 1.0, the sum of the products is equivalent to the sputtering rate. Therefore, the concentration of each element can be calculated by dividing by the sputtering rate.
Figure 2. Concentration-correcting step in making the calibration curve for silicon.
a. Raw calibration data. b. Sputtering-rate corrected calibration.
The key points in converting the sputtered depth to sputtering time are the sputtered mass and the density. The sputtered mass can be obtained from the sputtering rate and sputtering time. In the SIMR method, the density is calculated as a weighted average of the density of the pure elements, according to their concentrations in atomic percent. This method is essentially based on the assumption that all atoms, regardless of mass, occupy the same volume in a solid. This relation can be mathematically expressed as

\[ \frac{1}{\rho_b} = \sum C_n/(\rho_n) \]  \hspace{1cm} (4)

Where \( \rho_b \) is the density of the sample segment b and \( \rho_n \) is density of element n. \( C_n \) is the concentration of element n in sample segment b.

Another algorithm has also been adopted. The method used in the Surface Analysis Laboratory at Western Kentucky University is expressed as

\[ \rho_b = \sum x_n \rho_n \]  \hspace{1cm} (5)

Where \( x_n \) is the fraction of element n in this sample segment b.

Through the above equations and assumptions, the calibration curves under certain conditions are established, so that the raw signals from the GD-AES technique can be utilized to perform quantitative depth profiling.

2. Depth Resolution

A large variety of applications of quantitative depth analysis by GD-AES have been documented. Metal coatings of various types make up the majority of the published applications. Typically the metal coating is applied to a steel substrate, in order to protect the steel from corrosion and act as a base for painting or other decorative finishes. Numerous studies concerning the metal alloy coatings have been reported in the literature. The coating mass and coating composition of these coatings can be obtained
through GD-AES analysis, and this information is essential to improve production processes and to assist in the development of new and improved coatings. In the field of coating surfaces, an important requirement is knowing the in-depth distribution of elements. One of the aims for surface analysis is therefore to assign a specific concentration to the exact depth position. In order to interpret depth profiles properly, using sputtering methods, it is important to know the depth resolution.

Sputtering is “the ejection of target atoms following the impact of energetic ions and neutral atoms.”26 When dealing with the surface of complex multi-component solids, different components will sputter at different rates. Some elements will sputter preferentially, resulting in a change in surface composition. Finally, a steady state is reached through the conservation of mass, where elements are sputtered at a rate proportional to the underlying stoichiometry. The sputtering process will cause a crater in the investigated sample surface. For best depth resolution during depth-profiling, the bottom of the crater formed during sputtering should be as flat as possible. However, the impact of the argon ions and the subsequent sputtering of the sample surface are fairly random processes. This situation will result in some area being eroded by chance more quickly than others, thus a crater bottom in the shape of slightly concave or convex is produced.

Theoretically, the depth for steady state sputtering is in the order of nanometers at the relatively low energies employed in the Grimm lamp.27,28 In practice, the real depth resolution may decrease remarkably by physical and material specific effects. This fact also applies to GD-AES, where material erosion is not homogeneous over an area of a few tenths of mm² and reduces the real depth resolution enormously. Factors contributing to this fact include the sample material, the Grimm lamp geometry (diameter
of anode tube, distance between sample and anode) and the glow discharge lamp (GDL) parameters like pressure, voltage and current.

Instead of the statistical nature of the sputtering, the overall shape of the crater bottom is the biggest effect on depth resolution, because the curved crater bottoms will cause the sputtering occurring at a single time in different depths. In this study, the optimum conditions for a better depth resolution in the analysis of galvanized steel plates will be explored.

E. Purpose of This Study

Due to their excellent corrosion resistance, various types of galvanized sheet steels are used extensively in such diverse areas as automotive manufacturing, home appliances and construction industries. The plates may consist of pure Zn or some Zn-base alloy with coating thickness in the of range 5-20 μm. These types of materials have become the technically and economically most important application of GD-AES depth profile analysis to date.

Galvanized steel plates were investigated in this study. There was already a complete method for metal alloy depth analysis in the Surface Analysis Laboratory at Western Kentucky University. The generally adopted experimental parameters work well on most samples. However, whether these parameters are applicable in the analysis of galvanized steel plates are in doubt. One hundred repeat runs were carried out using these parameters, then the shapes of crater bottoms were examined. The optimum conditions for measuring the galvanized steel plates were developed thereafter through changing the lamp parameters. Finally, a calibration curve for quantitative analysis of zinc was constructed, and several unknown samples were quantitatively analyzed.
II. EXPERIMENTAL

A. Instrumentation

1. SA-2000 Surface Analyzer

   The glow discharge source used in the SA-2000 spectrometer is a water-cooled standard 4 mm Grimm Lamp. The sample is sealed on the lamp body by means of the o-ring. High purity (99.999%) argon gas is used as this discharge gas. The argon gas enters the lamp and leaves through two pumps, which maintain the vacuum condition for the system.

   The SA-2000 spectrometer is a 0.4 m meter direct reader that provides 0.55 nm/mm first order dispersion, which is shown schematically in Figure 3. The spectra are in range of 150 to 456 nm. This classical Paschen-Runge configured spectrometer permits up to twenty-eight output channels. The elements which the SA-2000 can currently analyze include: Ag, Al, As, C, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb, S, Se, Ti, W, Zn and Zr. Raw intensities versus time are collected using a computer equipped with fast digital signal processing hardware.

2. Microscope

   The microscope employed to observe the shape of sputtered craters is the Olympus U-RLA vertical illuminator. The images can be magnified 20, 50, 100, 200 and 500 times. In this study the 50-times-magnified images were employed to observe the crater shapes.
Figure 3. The classical Paschen-Runge configured SA-2000 spectrometer.
3. **Polaroid Micro Camera**

   The Polaroid Micro camera was used to provide instant photographs of the sputtered craters observed by means of microscopes. The camera is simple to operate and is easily attached to the microscope’s viewing tube, in place of the eyepiece. The camera automatically adjusts the exposure time according to the brightness. Polaroid film 331 was employed and develops automatically in normal room lighting in four to five minutes.

**B. Materials Used**

   The materials studied in this study were commercial coated steel products, which were obtained from the Machine Shop, Western Kentucky University. Samples consisted of steel with zinc coating, called galvanized steel, with a typical coating thickness of the order of 2–5 μm.

   Three standards used to construct the calibration curve for zinc were CKD\247, CKD\248A and NIST\C1153A. These standards contain a large number of elements with certified concentration. Especially, the concentration of zinc in each standard is listed in Table 1.

   **Table 1. Zinc Concentrations of Standards Using for Calibration**

<table>
<thead>
<tr>
<th>Standard</th>
<th>Concentration (%)</th>
<th>Uncertainty (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CKD\247</td>
<td>0.013</td>
<td>0.00070</td>
</tr>
<tr>
<td>CKD\248A</td>
<td>0.007</td>
<td>0.00011</td>
</tr>
<tr>
<td>NIST\C1153A</td>
<td>0.005</td>
<td>--------</td>
</tr>
</tbody>
</table>
C. Experimental Procedure:

1. Investigation of the Grimm Lamp Operation Parameters

With respect to the SA-2000 Surface Analyzer used in this study, the general Grimm lamp operation parameters adopted for metal alloy depth analysis are the following: current = 20 mA and voltage = 700 V. These parameters work quite well on most metal alloy samples. However, whether they are applicable to the analysis of galvanized steel plate is in doubt, thus one hundred repeat tests were carried out under the condition of 20 mA and 700 V.

The sputtering time is controlled by means of stopping the sputtering at the interface, which was achieved by aborting analysis when the intensity of zinc emission line decreases down to 10% of its original intensity. When the sample was taken from the O-ring, the resultant craters were subjected to microscopic analysis and the pictures were taken with the Polaroid Micro camera.

2. Optimization of Depth Resolution

The depth resolution is defined as the difference of depth between different locations over the average depth of the crater. Generally the crater is shown as flat, concave or convex shape. Some investigations with the LECO Surface Analyzer SA-2000 were carried out to clear up the influence of glow discharge pressure, voltage and current in optimizing the erosion of galvanized steel.

In order to determine the effect of pressure on the resulting crater shape, the experiments in constant current (20 mA) mode under different pressures were conducted first. With a constant current as 20 mA, the pressure was changed in the range of 5.0 torr to 1.5 torr. Under each condition, the galvanized steel samples were measured at least 20 times, so that a reliable conclusion can be made.
The optimum pressure for a desirable depth resolution was determined from the above experiments. Then at the determined optimum pressure condition, which is 2.0 torr, the voltage and the current of the Grimm lamp were changed in the range of 700 V to 1200 V, 18 mA to 25 mA, respectively, in order to obtain the optimum voltage and current range.

The determined optimum lamp operation parameters will be used in the following study.

3. Semiquantitative Approach

It is an essential step in the quantification procedure to construct a calibration curve, in order to convert the raw signals from the GD-AES to the concentration as a function of sputtered depth. The work is fulfilled in our study by measuring several standard materials with known concentrations of zinc. Then several galvanized steel plate samples were investigated, in order to obtain the information concerning the coating thickness and zinc distribution in the different layer of samples.
III. RESULT AND DISCUSSION

A. Investigation of Grimm Lamp Operation Parameters

The bombardment of argon ions on the galvanized steel plate will result in a crater on the plate surface. It has been realized that for GD-AES sputtering of metallic coatings on substrates real depth resolution mainly depends on the form of erosion crater.\(^{29}\) The raw data from GD-AES, which is intensity-time profile, can be received as a suitable qualitative in-depth analysis provided that the sputtering results in a relatively flat erosion crater shape, so that the sputtering taking place at a single time is in the same depth. As regards the galvanized steel samples investigated in this study, if the crater is sputtered evenly, there is no zinc remaining on the crater surface, otherwise the dark zinc clusters will appear somewhere on the crater.

One of the photographs of the craters is shown in Figure 4. As illustrated, the crater is in the form of concave. The dark circular zinc cluster is clearly observed on the rim of the crater. In the center of the crater is iron, the base metal, which appears as light color region in the photograph.

All the craters resulting from the 100-time repeat runs are analogous to that shown in Figure 4. Even without the microscope, the black zinc cluster on the rim of the crater is perceptible.

A conclusion that can be drawn from this set of experiments is that the general parameters adopted for the SA-2000 is not suitable for the analysis of the galvanized
Figure 4. The crater shape obtained under the constant current-voltage condition of 20 mA and 700 V.
steel plates. Therefore it is necessary to optimize the lamp operation parameters, in order to achieve a better depth resolution for the analysis of galvanized steel plates.

B. Optimization of the Experimental Parameters

The three main parameters for monitoring and controlling the glow discharge lamp are current, voltage and pressure. There is a relationship between these three parameters as follows:

\[ V_g = V' + 4k_i^1 / \pi D^m P_g^s \]  

(6)

Where \( V_g \), \( i_g \) and \( P_g \) stand for the maintaining voltage, current and pressure during the sputtering process, respectively.

\( V' \) is the threshold voltage. No current flows until \( V_g \) exceeds \( V' \).

\( D \) is the diameter of the anode. The \( k \), \( r \), \( m \) and \( s \) are four constants, which are matrix dependent.

The four matrix-dependent constants involved in equation 6 determine that the relation between current, voltage and pressure will vary with the matrix. Consequently, it is impossible to keep all three parameters constant for during calibration, analysis and depth-profiling processes. For given values for two of the parameters, the lamp will find its own value for the third, a value which can vary significantly from one sample matrix to the another or from one depth to the next as the matrix changes. Hence the lamp must be operated in one of three different modes: with current, voltage or pressure variable.

Considering the effect of pressure on the shapes of the erosion craters, experiments optimizing the pressure under current-pressure-constant control mode were first conducted. For a constant current of 20 mA, different pressures were chosen between 5.0 torr and 1.5 torr. Figure 5 illustrates one of the erosion craters under the
Figure 5. The crater shape obtained under the constant current-pressure condition of 20 mA and 3.0 torr.
pressure of 3.0 torr. The dark zinc cluster is clearly observed on the rim of the crater, and the shape of the crater can be described as slightly concave. Actually, this photograph represents most of the crater shapes under the condition of 3.0 torr or a higher pressure, including 4.0 torr and 5.0 torr. As mentioned previously, under the constant current and vacuum condition, the voltage of the lamp was varied during the sputtering processes as the different layer of the sample was penetrated. As reflected from Figure 6, the voltage during the sputtering process was in the range of 470 to 500 V under the condition of 20 mA current and 3.0 torr pressure. From equation 6, a higher pressure will result in a lower voltage. When the pressure is changed to 5.0 torr, it is found that the voltage falls into the range of 330 to 360 V, as inferred from Figure 7. It seems that the high pressure, which corresponds to the lower voltage from equation 6, will promote the formation of the concave crater.

When the pressure is in the range of 2.0 to 2.5 torr, the resulted craters have a nearly flat bottom. Figure 8 shows one of the even burns. Unlike the previous cases in which the dark zinc cluster gathered around the rim of the craters, in this photograph it is shown that some dark spots scatter on the surface of crater evenly. Figure 9 is a photograph of another erosion crater produced under the condition of 20 mA and 2.0 torr. Dark zinc clusters appear only randomly on the crater bottom. The remaining zinc dots in the bottom of crater may be due to the roughness of the base steel surface. The voltage under the condition of 20 mA and 2.0 torr is in the range of 800 V to 1800 V according to the diagnostics diagram, presented in Figure 10. However, the signals become unstable when the voltage approaches 1400 V, since it is in the range of spark discharge.

Despite the appearance that the lower voltage pressure favors the formation of craters with flat-bottoms, it cannot be unequivalently said that the lowest available
Figure 6. The response of voltage during the sputtering process under constant current-pressure condition of 20 mA and 3.0 torr
Figure 7. The response of voltage during the sputtering process under constant current-pressure condition of 20 mA and 5.0 torr.
Figure 8. The crater shape obtained under the constant current-pressure condition of 20 mA and 2.0 torr.
Figure 9. The crater shape obtained under the constant current-pressure condition of 20 mA and 2.0 torr.
Figure 10. The response of voltage during the sputtering process under constant current-pressure condition of 20 mA and 2.0 torr.
pressure is desirable. When the pressure is set at 1.5 torr, the corresponding voltage is extremely high. Under such conditions, the intensity of the signal of the examined sample is too unstable to render a reliable result.

The optimum pressure to obtain a better depth resolution for the analysis of galvanized steel is in the range of 2.0 to 2.5 torr. The next aim of this study is to determine the optimum voltage and current. Under voltage-pressure constant conditions, the pressure was fixed at 2.0 torr, and voltage was set at 700, 800, 900, 1000, 1100 and 1200 V, respectively. Erosion craters with a flat bottom were observed when the voltage in the range of 900 to 1200 V. Figure 11 reflects one such flat crater. The samples were also investigated under voltages higher than 1200 V; however, the signals became unstable under such conditions, as observed from the intensity versus time plot. In addition, the shape of crater-bottoms obtained under potentials higher than 1200 V are shown as convex. An example of a convex crater bottom is clearly illustrated in Figure 12. In the event that the potential is lower than 900 V, concave crater bottoms were obviously observed. This result is in agreement with the information obtained from other researchers' work.

To optimize the current when the pressure is fixed at 2.0 torr, the currents in the range of 18 mA to 25 mA were examined. It was found that the signals of the intensities became considerably unstable when the current is 22 mA or higher, while the crater was obviously unevenly sputtered when the current is set at 18 mA, as shown in Figure 13. From these results it can be stated that, for practical work, lamp currents between 19 mA and 21 mA are preferable to obtain a nearly flat material erosion by GD-AES sputtering.
Figure 11. The crater shape obtained under the constant voltage-pressure condition of 1000 V and 2.0 torr.
Figure 12. The crater shape obtained under the constant voltage-pressure condition of 1300 V and 2.0 torr.
Figure 13. The crater shape obtained under the constant current-pressure condition of 18 mA and 2.0 torr.
As mentioned above, the emission yield is a function of voltage and current during the sputtering process. In order to avoid the influence of emission yield therefore to simplify the experiments, the constant current-voltage condition was chosen as the operation mode for the later tests. The current will be set at 20 mA and the voltage will be fixed at 1000V as well. Such current and voltage values will lead to a pressure in the range of 2.0 to 2.2 torr during the test as shown in Figure 14.

To obtain a crater with a flat bottom, the argon ions bombarding the sample should be evenly distributed and kept constant across the surface. In fact, the number of argon ions will vary with the voltage distribution in the cathode dark space, in particular, and how far this voltage extends into the dead region opposite the annular face of the anode. For a given matrix and a given current, too high a voltage at the sides of the crater will result in an overall convex crater, whereas too low a voltage will cause a concave crater. In general, under good conditions the depth resolution is about 15% of the depth.4

The formation of the convex crater can be explained by the distribution of the electric field in the discharge lamp. Figure 15 shows the equipotential surfaces by 100 V steps in the Grimm-type glow discharge lamp. Close to the anode tube wall, the electric field strength is higher so the bombarding ions receive a higher energy during a shorter time and on a shorter path. In the case that the lower potential is adopted in the analysis, the difference between the electric field strength on the center and the rim is negligible. However, such difference becomes considerable and will lead to the formation of the convex craters. Dezso Demeny in Kossuth Lajos University investigated the influence of anode geometry on electric field distribution and crater profile.29 An equation is proposed from their study to describe the relationship between the potential U and the radius of the crater.
Figure 14. The response of pressure during the sputtering process under constant current-voltage condition of 20 mA and 1000 V
Figure 15. Equipotential surface by 100 V in the Grimm type glow discharge lamp.
\[ U = ae^{bR} + c \]

(7)

Under this equation, the depth of crater is calculated as a function of the radius of crater. The equation is described as

\[ h = ae^{bR} + c \]  

(8)

Where \( h \) stands for the depth of the crater in \( \mu m \),

\( R \) is the radius of the crater in mm,

\( a, b, c \) are constant.

It is suggested from the above equation that the depth of the crater is deeper on the rim no matter how much the potential is. According to their conclusion, the increase of the high burning voltage at constant pressure results in a relatively high difference in sputtering rate depending on the burning spot radius. Therefore, a reduction of the discharge voltage should lead to a decreased convexity of the crater. The increase in the diameter of the anode tube to a reasonable limit and the use of a potential - free restrictor as a spacer for the anode tube are recommendable measures to obtain the flat crater.\(^{30}\)

A similar conclusion was drawn from the study of J. Angeli and co-workers.\(^{31}\) A common 4 mm GD lamp with a distance of 0.2 mm between the anode tube and the cathode was used in their study to determine the shape of the erosion crater for different GD lamp parameters. All craters showed a convex shape, with \( T_e/T_c \) (depth at the crater edge and the center) greater that 1.0. Higher voltages increase this convex nature of \( T_e/T_c \) to a value of approximately 2. In the low range of 600 V a value of 1.2 is obtainable, which signifies a nearly flat erosion.

From both our study and other researchers’ work, it was shown that erosion craters in a concave shape would appear provided that the discharge potential is too low.
However, no explanations of this phenomenon have been found in the literature review. In my opinion, the formation of a concave crater under a low discharge potential may be attributed to the pressure in the discharge lamp. From equation 6 the pressure will increase with a decreased potential if the current is kept constant. Higher pressure represents more argon atoms present in the lamp. As mentioned above, there is a sputtering-depositing equilibrium for the sputtered materials in the lamp during the discharge process. In the view of statistics, the atoms at the center of the crater should have more chance to be sputtered than those located around the rim of the crater, because the vertical wall of the crater prevents the atoms on the rim from sputtering away.

The geometry of the anode also has significant effect on the depth resolution. J. Angeli carried out experiments using different anode tubes with diameters of 4 mm and 8 mm. The relative depth resolution ($\Delta z/z$) is used to interpret the depth profile, in which $\Delta z$ is defined as depth difference in the profile between 84% and 16% of signal maximum at the interface region and $z$ is the total thickness. The 4 mm GDL shows better relative depth resolution values for the same settings. With a common 4 mm glow discharge lamp to measure the ZnNi-coatings in a thickness range of some microns, a relative depth resolution between 0.13 and 0.15 is attainable. This data means an absolute depth resolution of approximate 130 nm at 1 µm depth and of 750 nm at 5 µm depth. Such a conclusion is consistent with the results obtained from the study of R. Payling.

Besides the attempt to avoid the formation of curved sputtering crater bottoms, some researchers in Germany advanced a new deconvolution technique to separate effects of an uneven erosion crater shape. This iterative deconvolution method for the quantification numerically takes into account the curved erosion crater bottom. Input data are the calibrated mass-time profile, the partial densities of the sample constituents.
and the measured final shape of the sputtering crater. This new technique may open up the way to significantly improve the depth profile analysis using GD-AES.

C. **Semiquantitative Approach**

Using the optimized conditions (current of 20 mA and voltage of 1000 V) determined in the above experiments, a new method for analysis of zinc was developed. Three alloy samples that have low zinc concentrations were used as standard calibration materials. These standards and their concentrations are listed in Table 1. Since no sample with high zinc concentration was available in the Surface Analysis Laboratory, an electroplate steel received from the LECO corporation was used as a standard with high zinc concentration. The zinc concentration of the coating is assumed to be 99.9%.

There are eleven elements in total that can be detected by this method. The wavelengths used to characterize the individual elements are listed in Table 2.

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength (nm)</th>
<th>Element</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>165.701</td>
<td>P</td>
<td>177.499</td>
</tr>
<tr>
<td>Co</td>
<td>345.351</td>
<td>S</td>
<td>10.731</td>
</tr>
<tr>
<td>Cr</td>
<td>267.716</td>
<td>Si</td>
<td>288.158</td>
</tr>
<tr>
<td>Fe</td>
<td>371.994</td>
<td>Ti</td>
<td>338.289</td>
</tr>
<tr>
<td>Mg</td>
<td>383.829</td>
<td>Zn</td>
<td>330.294</td>
</tr>
<tr>
<td>Ni</td>
<td>341.477</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
From our experiments, it was demonstrated that the thickness of the zinc coating on the galvanized steel sample is approximately 2 μm. It takes approximately 30 seconds to penetrate the zinc coating to reach the Zn-Fe interface under the test conditions. Before data acquisition, other standard samples will be preburned for 60 seconds in order to eliminate the influence of any contaminated surface. However, in the case of this electroplate coating, the preburn time was reduced to 20 seconds because of the limited thickness of the zinc layer. Each of these four samples was measured three times. The intensity-time profiles, in which the spectral line intensities were presented as a function of erosion time, were obtained. Using Multi-Analyte Fit program, which was designed by Dr. Harper in the Department of Physics in Western Kentucky University, the sputtering rate for each standard samples was calculated and a corrected calibration curve for zinc analysis was constructed thereafter. This calibration curve is shown in Figure 16.

With this calibration curve, several galvanized steel plate samples were qualitatively and quantitatively analyzed. The surfaces of the investigated galvanized steel plates were carefully cleaned using methanol prior to analysis. Each sample was tested 5 times under the exactly same experiment conditions to obtain comparable results. The distribution of zinc concentration at different layer in these samples is presented in Table 3.

First, the thickness of zinc coatings for these investigated samples is determined from the corresponding depth-concentration profile. The galvanized steel used in this study can be considered as a substrate comprising iron coated with a layer comprising zinc. It is predicable that the profiles of the emission intensities will change, especially at the interface between substrate and layer, when the emission lines of Fe and Zn are
**Zn: 330.294**

**Figure 16. Calibration curve for zinc.**

<table>
<thead>
<tr>
<th>Standard</th>
<th>Intensity</th>
<th>Calculated</th>
<th>Certified</th>
<th>Difference</th>
<th>% Error</th>
<th># Runs</th>
<th>Std. Dev.</th>
<th>Weight</th>
<th>Sputter Rate</th>
<th>Weight Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>WANGGALVANEAL</td>
<td></td>
<td></td>
<td>99.90</td>
<td>0.00000316</td>
<td>0.0003220</td>
<td>3</td>
<td>0.06</td>
<td>1.000</td>
<td>0.2696</td>
<td>1.000</td>
</tr>
<tr>
<td>CKD247</td>
<td>0.0000206</td>
<td>0.000025</td>
<td>0.000023</td>
<td>0.0000015</td>
<td>&gt;100</td>
<td>3</td>
<td>0.0004</td>
<td>1.000</td>
<td>0.0200</td>
<td>1.000</td>
</tr>
<tr>
<td>CKD248</td>
<td>0.000479</td>
<td>0.00050</td>
<td>0.00050</td>
<td>0.0000015</td>
<td>&gt;100</td>
<td>3</td>
<td>0.00006</td>
<td>1.000</td>
<td>0.0237</td>
<td>1.000</td>
</tr>
<tr>
<td>NISTC1153A</td>
<td>0.01038</td>
<td>-0.0001</td>
<td>0.00000</td>
<td>0.00004</td>
<td>&gt;100</td>
<td>3</td>
<td>0.00001</td>
<td>1.000</td>
<td>1.347</td>
<td>1.000</td>
</tr>
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</table>
Table 3. The Distribution of Zinc in Different Layers.

<table>
<thead>
<tr>
<th>Sample 1</th>
<th>0.4-0.5 μm</th>
<th>0.7-0.8 μm</th>
<th>1.0-1.1μm</th>
<th>1.5-1.6 μm</th>
<th>2.0-2.1μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 1</td>
<td>96.731</td>
<td>97.552</td>
<td>98.366</td>
<td>98.932</td>
<td>98.926</td>
</tr>
<tr>
<td>Run 2</td>
<td>99.322</td>
<td>99.399</td>
<td>99.288</td>
<td>99.068</td>
<td>98.739</td>
</tr>
<tr>
<td>Run 3</td>
<td>99.335</td>
<td>99.376</td>
<td>99.331</td>
<td>99.239</td>
<td>99.139</td>
</tr>
<tr>
<td>Run 4</td>
<td>95.888</td>
<td>97.066</td>
<td>98.115</td>
<td>98.779</td>
<td>98.815</td>
</tr>
<tr>
<td>Run 5</td>
<td>98.126</td>
<td>98.396</td>
<td>98.144</td>
<td>98.439</td>
<td>98.674</td>
</tr>
<tr>
<td>Average</td>
<td>97.880</td>
<td>98.358</td>
<td>98.649</td>
<td>98.891</td>
<td>98.859</td>
</tr>
<tr>
<td>% RSD</td>
<td>1.578</td>
<td>1.071</td>
<td>0.619</td>
<td>0.308</td>
<td>0.185</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample 2</th>
<th>0.4-0.5 μm</th>
<th>0.7-0.8 μm</th>
<th>1.0-1.1μm</th>
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<th>2.0-2.1μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 1</td>
<td>96.390</td>
<td>97.465</td>
<td>98.158</td>
<td>98.611</td>
<td>98.747</td>
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<tr>
<td>Run 2</td>
<td>98.348</td>
<td>98.914</td>
<td>98.949</td>
<td>98.999</td>
<td>98.885</td>
</tr>
<tr>
<td>Run 3</td>
<td>98.769</td>
<td>99.002</td>
<td>98.880</td>
<td>98.377</td>
<td>97.233</td>
</tr>
<tr>
<td>Run 4</td>
<td>97.718</td>
<td>98.419</td>
<td>98.512</td>
<td>98.372</td>
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<tr>
<td>Run 5</td>
<td>98.995</td>
<td>99.426</td>
<td>99.417</td>
<td>99.096</td>
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</tr>
<tr>
<td>Average</td>
<td>98.044</td>
<td>98.645</td>
<td>98.783</td>
<td>98.691</td>
<td>98.391</td>
</tr>
<tr>
<td>% RSD</td>
<td>1.066</td>
<td>0.761</td>
<td>0.481</td>
<td>0.346</td>
<td>0.686</td>
</tr>
</tbody>
</table>

---Continued---
Table 3. (Continued)

<table>
<thead>
<tr>
<th>Sample</th>
<th>0.4-0.5 µm</th>
<th>0.7-0.8 µm</th>
<th>1.0-1.1 µm</th>
<th>1.5-1.6 µm</th>
<th>2.0-2.1 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 1</td>
<td>94.878</td>
<td>97.386</td>
<td>98.039</td>
<td>98.352</td>
<td>98.527</td>
</tr>
<tr>
<td>Run 2</td>
<td>94.057</td>
<td>97.694</td>
<td>98.365</td>
<td>98.261</td>
<td>98.388</td>
</tr>
<tr>
<td>Run 3</td>
<td>98.574</td>
<td>99.315</td>
<td>99.317</td>
<td>98.556</td>
<td>98.477</td>
</tr>
<tr>
<td>Run 4</td>
<td>98.335</td>
<td>98.525</td>
<td>98.553</td>
<td>98.818</td>
<td>98.880</td>
</tr>
<tr>
<td>Run 5</td>
<td>97.660</td>
<td>98.874</td>
<td>98.770</td>
<td>98.701</td>
<td>98.592</td>
</tr>
<tr>
<td>Average</td>
<td>96.701</td>
<td>98.359</td>
<td>98.573</td>
<td>98.585</td>
<td>98.573</td>
</tr>
<tr>
<td>% RSD</td>
<td>2.157</td>
<td>0.819</td>
<td>0.420</td>
<td>0.236</td>
<td>0.189</td>
</tr>
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<table>
<thead>
<tr>
<th>Sample</th>
<th>0.4-0.5 µm</th>
<th>0.7-0.8 µm</th>
<th>1.0-1.1 µm</th>
<th>1.5-1.6 µm</th>
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<tr>
<td>Run 1</td>
<td>98.773</td>
<td>99.082</td>
<td>99.173</td>
<td>98.870</td>
<td>96.060</td>
</tr>
<tr>
<td>Run 2</td>
<td>98.417</td>
<td>99.370</td>
<td>99.535</td>
<td>99.609</td>
<td>97.676</td>
</tr>
<tr>
<td>Run 3</td>
<td>96.805</td>
<td>98.636</td>
<td>99.343</td>
<td>99.012</td>
<td>96.786</td>
</tr>
<tr>
<td>Run 4</td>
<td>98.090</td>
<td>99.293</td>
<td>99.471</td>
<td>99.209</td>
<td>97.300</td>
</tr>
<tr>
<td>Run 5</td>
<td>95.139</td>
<td>98.239</td>
<td>99.974</td>
<td>98.755</td>
<td>98.046</td>
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<tr>
<td>Average</td>
<td>97.445</td>
<td>98.924</td>
<td>99.499</td>
<td>99.091</td>
<td>97.174</td>
</tr>
<tr>
<td>% RSD</td>
<td>1.527</td>
<td>0.483</td>
<td>0.301</td>
<td>0.338</td>
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Table 3. (Continued)

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<th>Sample 6</th>
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<td>1.0-1.1μm</td>
<td>1.5-1.6 μm</td>
</tr>
<tr>
<td>Run 1</td>
<td>98.482</td>
<td>98.943</td>
<td>98.884</td>
<td>98.680</td>
</tr>
<tr>
<td>Run 2</td>
<td>98.792</td>
<td>98.792</td>
<td>98.782</td>
<td>98.698</td>
</tr>
<tr>
<td>Run 5</td>
<td>98.707</td>
<td>98.901</td>
<td>98.861</td>
<td>98.628</td>
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<tr>
<td>Average</td>
<td>98.942</td>
<td>99.047</td>
<td>98.937</td>
<td>98.695</td>
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<tr>
<td>% RSD</td>
<td>0.406</td>
<td>0.260</td>
<td>0.144</td>
<td>0.058</td>
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Table 3. (Continued)

<table>
<thead>
<tr>
<th>Sample</th>
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<th>0.7-0.8 µm</th>
<th>1.0-1.1 µm</th>
<th>1.5-1.6 µm</th>
<th>2.0-2.1 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 1</td>
<td>97.624</td>
<td>97.587</td>
<td>97.906</td>
<td>98.472</td>
<td>98.844</td>
</tr>
<tr>
<td>Run 2</td>
<td>98.156</td>
<td>98.764</td>
<td>98.756</td>
<td>98.655</td>
<td>98.611</td>
</tr>
<tr>
<td>Run 3</td>
<td>97.692</td>
<td>98.561</td>
<td>98.571</td>
<td>98.575</td>
<td>98.647</td>
</tr>
<tr>
<td>Run 4</td>
<td>96.907</td>
<td>97.550</td>
<td>97.855</td>
<td>98.080</td>
<td>98.452</td>
</tr>
<tr>
<td>Run 5</td>
<td>97.641</td>
<td>98.747</td>
<td>98.740</td>
<td>98.555</td>
<td>98.306</td>
</tr>
<tr>
<td>Average</td>
<td>97.604</td>
<td>98.242</td>
<td>98.366</td>
<td>98.467</td>
<td>98.572</td>
</tr>
<tr>
<td>% RSD</td>
<td>0.458</td>
<td>0.631</td>
<td>0.456</td>
<td>0.230</td>
<td>0.207</td>
</tr>
</tbody>
</table>

Sample 8

| Run 1   | 98.230     | 98.595     | 98.471     | 97.857     | 97.227     |
| Run 5   | 97.431     | 99.175     | 99.456     | 99.234     | 98.695     |
| Average | 98.516     | 99.251     | 99.337     | 99.155     | 98.500     |
| % RSD   | 0.733      | 0.397      | 0.491      | 0.746      | 0.863      |
measured during sputtering. Figures 17, 18 and 19 are the depth-concentration profiles for samples 1, 2 and 3, respectively. As clearly shown in these figures, the zinc concentration, which is presented as analyte weight percent, was constant for the first several micrometers. Then the concentration of zinc drops abruptly and the concentration of iron increase substantially, representing that the erosion approaches the Zn-Fe interface. The thickness of the zinc coating is defined as the thickness where no significant iron signal appears, because zinc protected iron from being eroded. The results revealed the different thickness of zinc coatings of these samples. For instance, the zinc coating thickness of sample 1 is 2.2 μm, whereas that of samples 2 and 3 is 1.5 μm and 4.0 μm, respectively. In addition, the analysis reveals that trace amounts of impurities such as Mg, Cu, etc., present in the zinc coating.

Another quantification completed concerned the in-depth distribution of the elements. Such information is of vital importance for the coating quality control in the industry. Sample 1 is employed as an example for the depth profile analysis. The concentration of zinc at the various depths of the steel plate is readily known from the concentration-depth profile. For example, the average zinc concentration is 97.880% in the layer from 0.4-0.5 μm; 98.358% in the 1.0-1.1 μm; 98.649% in the 1.0-1.1 μm, 98.891% in the 1.5-1.6 μm and 98.859% in the 2.0-2.1 μm layer. The percent relative standard deviation (RSD) of the concentrations at different layer beyond 2.1 μm is 0.380%. It can be concluded from the above analysis that the zinc is evenly distributed in the coating, in another words, the coating is rather homogenous.

Another comparison was conducted in order to prove the reproducibility of this method. Sample 1 is used as an example. As mentioned earlier, each sample was measured at different locations under same conditions. For the 5 repeat runs, the zinc
Figure 17. The concentration-depth profile for sample 1.
Figure 17. The concentration-depth profile for sample 1.

Figure 18. The concentration-depth profile for sample 2.
Figure 19. The concentration-depth profile for sample 3.
concentrations at depth of 1.0-1.1 µm are 98.366%, 99.288%, 99.331%, 98.115%, 98.115% and 98.144%. The values are quite similar, and the RSD for them is 0.619%. Similar to other investigated galvanized steel plates, the RSDs of the results from the five repeat runs are less than 1.0%. This fact indicates that the plate is uniform and the data obtained using this method is reproducible and this technique is reliable.
IV. FURTHER STUDY

The GD-AES system with a dc source has versatile applications in solid sample analyses. However, the dc power mode limits the use of GD-AES to only the conductive samples. The analysis of non-conductive samples by means of dc GD-AES, in most cases, involves the mixing of the samples with a suitable conductive host matrix material, such as graphite or copper, thus not allowing in-depth profile analysis. The GD-AES system with a rf source allows the sputtering of both conductive and non-conductive samples, thus it is expected to be capable of depth profiling of non-conductive samples provided that the proper calibration procedure is available.

Several empirically based quantitative schemes are now available for the more established dc-GD-AES technique; however, no comprehensive theory has been available for quantitative depth profiling for GD-AES with a rf source until now. It is important to develop a quantification procedure before rf GD-AES can reach its full potential.

Since many of the lamp parameters are comparable in both dc and rf modes and therefore the analytical characteristics of the two methods are similar, it seems reasonable that the quantitative methods developed for dc GD-AES would be a good starting point for rf GD-AES.

Similar to what is encountered in the quantification procedure for dc GD-AES, the intensities should be converted into concentrations while the time scale has to be converted into a depth scale for the depth-analysis using rf GD-AES. Payling and co-
workers have proposed a theory to fulfill the above task. Unlike the theory developed in the SIMR, it is assumed that the emission yield depends on only the pressure. If all the calibration and analysis are conducted with constant pressure and constant rf power, then the relationship between emission intensity and concentration can be expressed by

$$I_x = K_x \cdot c_x \cdot SR + b_x$$

(9)

Where $K_x$ is the calibration constant, $SR$ is the sputtering rate,

$b_x$ is the background signal.

The constant $K_x$ in equation 9 is an elemental sensitivity factor. Values of $K_x$ have been estimated for a wide range of elements using equation 9 by linear regression to measurement of $I_x/SR$ versus $c_x$.

Five standards were used in the experiments. They are NIST steels 1262a-1264a and MBH zinc/aluminum alloys 0336ZN2 and 0336ZN3. These standards contain a large number of elements with certified concentrations. More important, these standards are both iron and zinc matrices, so a more severe test of the theory is obtained than by results from a single matrix. The result illustrates the high degree of linearity. The dc and rf sensitivity factors relative to iron for 17 elements are shown in Table 4.

Based on previous work, the qualitative intensity-time profile of the metallic coated samples can be converted to the quantitative depth profile. Although the qualitative profile show differences in dc and rf modes, the quantitative profiles are remarkably similar. This ability to give comparable quantitative depth profiles in dc and rf without any adjustable parameters between the two modes in the computer program, despite the very different lamp conditions of current and voltage operating in the two modes, proves the theory is more reliable.
Table 4. Elemental Sensitivity Factors Relative to Iron.

<table>
<thead>
<tr>
<th>Element</th>
<th>Line (nm)</th>
<th>dc</th>
<th>rf</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>156.1</td>
<td>0.021 ± 0.004</td>
<td>0.021 ± 0.001</td>
</tr>
<tr>
<td>Al</td>
<td>396.1</td>
<td>1.5 ± 0.1</td>
<td>1.4 ± 0.2</td>
</tr>
<tr>
<td>Si</td>
<td>288.1</td>
<td>0.15 ± 0.02</td>
<td>0.17 ± 0.03</td>
</tr>
<tr>
<td>P</td>
<td>177.4</td>
<td>0.08 ± 0.02</td>
<td>0.09 ± 0.02</td>
</tr>
<tr>
<td>S</td>
<td>180.7</td>
<td>0.5 ± 0.2</td>
<td>0.6 ± 0.2</td>
</tr>
<tr>
<td>Ti</td>
<td>337.2</td>
<td>2.0 ± 0.2</td>
<td>2.5 ± 0.4</td>
</tr>
<tr>
<td>Cr</td>
<td>425.4</td>
<td>26 ± 2</td>
<td>22 ± 2</td>
</tr>
<tr>
<td>Mn</td>
<td>403.4</td>
<td>4.8 ± 0.3</td>
<td>3.9 ± 0.3</td>
</tr>
<tr>
<td>Fe</td>
<td>371.9</td>
<td>1.0 ± 0.2</td>
<td>1.0 ± 0.2</td>
</tr>
<tr>
<td>Co</td>
<td>345.3</td>
<td>2.7 ± 0.7</td>
<td>2.7 ± 0.9</td>
</tr>
<tr>
<td>Ni</td>
<td>341.4</td>
<td>1.6 ± 0.1</td>
<td>1.6 ± 0.1</td>
</tr>
<tr>
<td>Cu</td>
<td>327.3</td>
<td>2.7 ± 0.2</td>
<td>2.5 ± 0.2</td>
</tr>
<tr>
<td>Zn</td>
<td>213.9</td>
<td>0.12 ± 0.02</td>
<td>0.12 ± 0.02</td>
</tr>
<tr>
<td>As</td>
<td>189.0</td>
<td>0.2 ± 0.1</td>
<td>0.2 ± 0.1</td>
</tr>
<tr>
<td>Mo</td>
<td>386.4</td>
<td>3.3 ± 0.5</td>
<td>2.8 ± 0.7</td>
</tr>
<tr>
<td>Cd</td>
<td>228.8</td>
<td>1.0 ± 0.3</td>
<td>1.1 ± 0.2</td>
</tr>
<tr>
<td>Pb</td>
<td>220.3</td>
<td>2.0 ± 0.9</td>
<td>2.0 ± 0.9</td>
</tr>
</tbody>
</table>


More recently, some scientists in Spain carried out an investigation on the use of rf GD-AES for in-depth profile analysis of painted coatings.\textsuperscript{35} It is found that the emission yield depends on not only the pressure but also the excitation efficiency. Normally, the excitation efficiency will undergo appreciable change as the layer being sputtered changes.

Obviously, in depth-profile analysis in most cases it is not feasible to use a spectral line from a major element as an internal standard. A basic requirement for an internal standard is that its concentration remains constant throughout the experiment. Since the pressure is kept constant during the sputtering process, an Ar line can be used as an internal standard to correct for changes in emission yield.

Parker and coworkers performed a study concerning the determination of the factors effecting the emission yields for both metallic and nonconductive sample types using rf GD-AES source. The results follow predicted patterns as determined by Langmuir probe diagnostic studies of a similar source. In particular, discharge gas pressure is the key operating parameter as slight changes in pressure may significantly affect the emission yield of the analyte species. Rf power is less important and is shown to produce only relatively small changes in the emission yield over the ranges typically used in rf-GD analyses. These studies indicate that the quantitative analysis of layered materials, through depth-profiling, may be adversely affected if the data collection scheme, i.e. the quantitative algorithm, requires changing the pressure during an analysis to keep the operating current and voltage constant. A direct relationship is shown to exist between the Ar (discharge gas) emission intensity and that of sputtered species for nonconductors. This observance is used to compensate for differences in emission intensities observed in the analysis of various thickness of nonconductive samples. The
sputtered element emission signals are corrected based on the emission intensity of an Ar transition, implying that quantitative analysis of nonconductive samples is not severely limited by the availability of matrix match standards.

These studies are helpful in finding a proper procedure for the in-depth analysis using rf GD-AES. Some ideas are presented here for the further study concerning rf GD-AES.

Since the shape of the erosion crater will be the ultimate factor that will limit the depth resolution, the first step is to optimize lamp operation parameters (power, current, voltage and pressure) to obtain a flat crater profile for SA-2000 when a rf source is employed. The relationship between the current, voltage and pressure in an rf GD source is much more complicated than that in a dc GD source, and no theory concerning it has been proposed to date. In my view, the optimizing process could be similar to that used for dc GD-AES, in which one operation mode (usually the power-pressure constant mode is accepted in rf GD-AES) is chosen at first, then one parameter is fixed and the other is changed and examined in order to obtain the optimum working range. One can obtain from these tests not only the optimum experiment conditions but also some significant data revealing the interrelation among the three parameters in an rf power GD source.

With a dc source, the concave shape craters are usually observed under the condition of a higher pressure. In contrast, the shape of the erosion crater sputtered at a lower pressure is clearly more concave that at higher pressures if a rf power is adopted.\textsuperscript{37} The reason for this discrepancy is unclear, but will certainly form a key aspect in future studies of the rf-GD approach to depth profiling.

Once the optimum conditions are set, the following process is to construct the calibration curve under the optimum conditions. A series of standard samples with
different zinc concentrations covering the interested range will be used. The raw data obtained will be emission intensity versus time profiles. To obviate the effect of sputtering rate on the emission profiles, the analyte concentrations should multiply the corresponding sputtering rate to obtain the “corrected concentration.” The calculation of sputtering rate can follow the same procedure as mentioned in the earlier section by using Multi-Analyte Fit program. Then the emission intensities can be plotted versus “corrected concentration.” It would not be a surprise if this curve shows unacceptable scatter, and one remedy for this situation is the use of Ar line as internal standard as some researchers suggested. In depth profile analysis it is generally not possible to use a spectral line from a major element as an internal standard. However, argon (the discharge gas) is always present as the major element in the plasma. By ratioing analytical line intensities with an Ar channel, the variation in excitation efficiency can be compensated more or less. After the above corrections and improvements, a calibration curve reflecting the relationship between intensity and concentration will be established. Following the same approach as that used in a dc GD-AES, the conversion of sputtering time intensity into sputtering depth is rather easy.

With the established calibration curve, the in-depth analysis of conductive and nonconductive samples using rf GD-AES is feasible.
V. CONCLUSIONS

Based on the above study, the following conclusions can be drawn:

1. On the basis of the 100-time repeat runs on the galvanized steel plate, the general parameters adopted for the SA-2000 to analyze the metal alloy are not applicable to the analysis of galvanized steel plate, since the shapes of all the crater-bottoms resulting from the sputtering process are obviously concave.

2. The optimum lamp operation parameters for analysis of galvanized steel plate using the SA-2000 are as follows:
   
   Current: 19 - 21 mA
   
   Voltage: 900 – 1200 V
   
   Pressure: 2.0 –2.5 torr
   
   The results indicated that after optimization of the conditions, very flat crater profiles without accumulation of redeposited materials in the area of the crater rims could be obtained. With a flat crater shape, the sputtering occurring at a single time is in almost the same depth, so that a reliable concentration-depth profile can be obtained through the calibration.

3. Using the optimized parameters (current of 20 mA, voltage of 1000V), a calibration curve is constructed for qualitatively and quantitatively analyzing the zinc coating. The specific zinc concentration can be assigned to the exact depth position in the investigated sample with this calibration. Several galvanized steel plate samples were examined thereafter. From the depth-concentration profile,
the thickness of the coating and the distribution of zinc in different depths of the coating is obtained. The results indicate the homogeneity of the coating on the galvanized steel samples. Through the analysis of the RSD of the data from different runs on the same sample, the reproducibility of this method is estimated.
VI. BIBLIOGRAPHY


