

## REVIEW

# Quantitative depth profile analysis by glow discharge

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*(Received and accepted 1S November 1993)*

Abstract – The development of dc glow discharge spectrometry for depth profile analysis is reviewed. Different approaches to quantification of depth profile measurements into elemental concentrations vs depth are discussed. Methods for quantitative glow discharge optical emission spectrometry (GD-OES), based on the concept of emission yield (emission intensity/sputtered weight), are described in detail. The alternative quantification method developed at the Swedish Institute for Metals Research, which also incorporates compensation for variations in excitation parameters, is presented. Current work on GD mass spectrometry (GD-MS) for quantitative depth profile analysis is briefly reviewed. Several applications of quantitative GD spectrometry to metallic and non-metallic surface layers are presented. Some of the remaining problem areas with regard to quantification are discussed: reference materials, accuracy of the depth determination, influence of released gaseous species, and correction for background signals.

## 1. Introduction

THE FIRST work on depth profile analysis by glow discharge was published by GREENE and WHELAN [1] in 1973. The application was GaAs thin films. The same year, BELLE and JOHNSON [2] first demonstrated the possibility of using the glow discharge for depth profiling of metal alloys. Their work was also the first in which the Grimmtype source was used. In both of these pioneering works, the GD was utilized as a source for optical emission spectrometry, this still being the most commonly used technique for signal detection. In recent years, glow discharge mass spectrometry has also emerged as a powerful technique for depth profile analysis [3, 4]. In this paper, the acronyms GD-OES will be used for the former technique, and GD – MS for the latter.

Glow discharges exist in dc (direct current) and rf (radio frequency) varieties. The overwhelming majority of depth profile work to date has been done with dc sources, owing to the fact that rf systems have become commercially available only in the last few years. Today, there is a rapidly growing interest in rf sources, mainly due to their capability of sputtering non-conducting materials. However, it should be stated here that this paper deals only with work based on dc glow discharges; rf work will, hopefully, become the next chapter in this interesting development [5].

## 1.1 The Grimm source

In the majority of publications on depth profile analysis by GD-OES, the GD sources used are based on the design of GRIMM [6] from 1967. Although originally intended as an alternative to the spark source for routine bulk analysis (for which purpose it works splendidly), the Grimm GD has also proven to be an excellent tool for depth profile analysis. The principal layout of this source is provided in Fig. 1. The lamp body is normally at ground potential, and the water-cooled, isolated front plate is at negative potential during operation. The tubular-shaped anode fits tightly into the central opening of the front plate, and extends to approximately 0.2 mm distance from the front surface. The inner diameter of the anode is typically 8 mm, but anodes of 7, 5, 4, 2.5 and 1 mm diameter have also been used. The sample, which forms the cathode, is placed on the front plate, and sealed from the atmosphere by an O-ring of relatively soft material. When operated the lamp house is first evacuated for a few seconds by a rotary pump (pumpdown), after which time an argon flush valve is opened. After a few seconds to stabilize the pressure (preflush), the discharge is initiated by applying a voltage of typically 500-1000 V. The geometry of the lamp constricts the discharge physically to the inside of the anode tube (obstructed discharge). This is due to the fact that the distance between cathode and anode' is below the mean free path length of the electrons at some millibar pressure. 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

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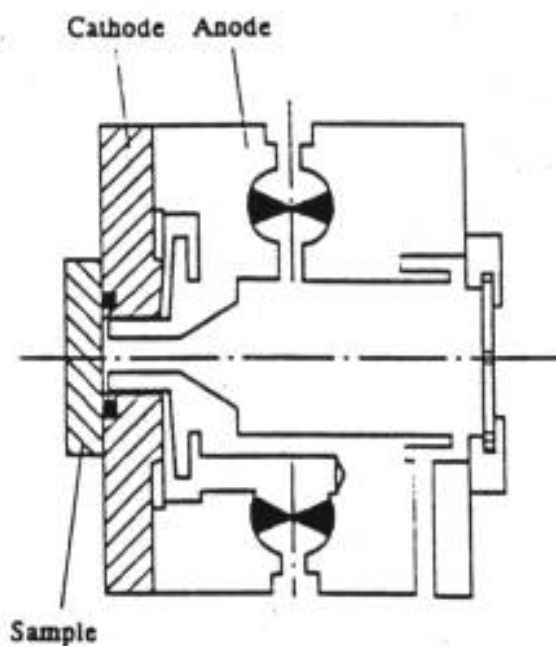


Fig. 1. Schematic diagram of the Grimm-type glow discharge source.

before being adsorbed on a cold surface inside the source. A substantial fraction of the sputtered atoms are redeposited on the sample surface, and a dynamic equilibrium is established at an "effective" sputtering rate, sometimes referred to as the sample loss rate. In this paper, the term "sputtering rate" is understood to be synonymous with "sample loss rate". While in the plasma, some sample atoms are excited and emit element-characteristic optical emission. A fraction of the sample atoms will also be ionized allowing detection by mass spectrometry.

With a relatively high current density of 50-500 mA/cm<sup>2</sup>, the penetration rate in a Grimm GD is typically in the range 1-10 μm/min. 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 (see Fig. 2). Thus, by recording the analytical signals (optical emission or ion current) as a function of sputtering time, an elemental depth profile is obtained.

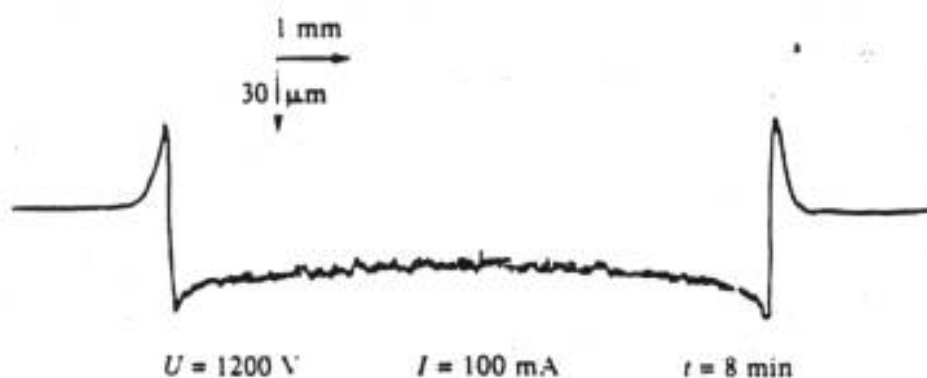


Fig. 2. Profilometer trace of sputtering crater.

## **1.2 Depth profile analysis with the Grimm source**

Although the pioneering work in this field was done by BELLE and JOHNSON [2] in the U.S.A., credit for the most important method development work goes to BERNERON and coworkers from the research institute IRSID in France [7-9]. Using a high vacuum polychromator ("direct reader") equipped with a Grimm-type source, they developed this system into an efficient, powerful tool for rapid depth profile analysis. Equally important, BERNERON showed that GD-OES is well suited for a wide range of industrially important applications, e.g. hot and cold rolled steels, nitrocarburized materials, phosphate coatings etc. Others who also contributed significantly to this development were HOCQUAUX and LEVEQUE [10, 11] and QUENTMEIER *et al.* [12]. The development work at IRSID was also the basis for the first commercially available GDL spectrometer systems (such as the Siemens Spectrumat 1000) with appropriate signal readout electronics and software for depth profile analysis.

## **2. The Quantification Problem**

The basic information obtained in a GD depth profile analysis is relative intensity from elemental detectors as a function of sputtering time. The quantification problem can be separated into two parts: (i) elemental concentrations: and (ii) sputtered depth. In the following treatment, the emphasis is on OES which, at present, is a more developed technique for quantitative depth profile analysis than MS. Quantification techniques for MS are briefly discussed in Section 3.4. For the elemental concentrations, there are well established methods for accurate quantification in bulk analysis. However, these methods are of limited use in depth profile analysis for a number of reasons. In bulk analysis, measurements are done on homogeneous samples of a rather well-defined matrix composition. Calibration of the analytical program is carried out with a set of reference materials of compositions similar to the unknown samples. Normally, a reference channel of the major element is used as a so-called internal standard. Consequently, a separate calibration is necessary for each material (alloy) type to be analysed. In depth profile analysis this approach is generally not applicable, since the different layers encountered in a depth profile often represent widely different material types (matrices). This can also be expressed by saying that depth profile analysis is a multi-matrix analytical problem, and therefore requires

a multi-matrix calibration method. This fact rules out the possibility of using any major element of the sample as an internal standard: consider for example a zinc coating on steel. Furthermore, the electrical parameters of the source (voltage, current) often vary considerably as layers of different composition are penetrated. Such variations affect the signal intensities, and must be accounted for in a complete quantification method.

Determination of the sputtered depth in GD depth profile analysis may at first sight appear to be an easy task, since it is relatively straightforward to measure the sputtering rates of specific materials accurately. In an important paper by BOUMANS in 1972 [13] it was shown that variations in voltage and current can also be effectively accounted for. Although such knowledge forms a solid base for depth calibration, to rely on a database of measured sputtering rates in order to determine sputtered depth is not sufficient for a generally applicable quantification model. The reason for this is that it is not practically feasible to measure sputtering rates of all the vast amount of material compositions that occur in real depth profile applications. Consequently, it is generally not possible to identify the composition of each segment of a real depth profile with some reference substance in a database. Yet another complication for the depth calibration procedure concerns the density of the sample material. Sputtering rates are most conveniently and accurately measured in terms of mass loss. For the depth calibration, it is necessary to obtain a value of the density of the material as well. As will be discussed in a later section, the estimate of the density constitutes a major imitation to depth calibration accuracy for certain applications.

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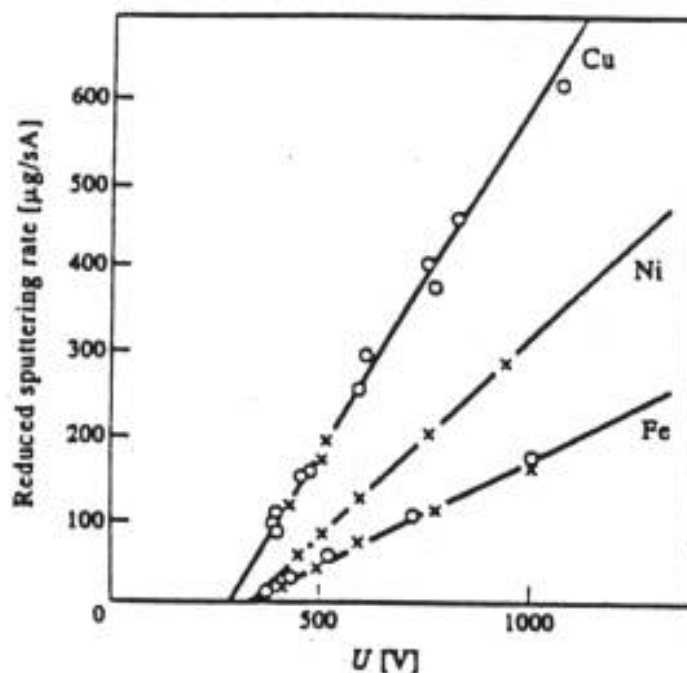


Fig. 3. Reduced sputtering rate vs voltage graphs for Fe, Ni and Cu.

## 2. 1. Early work on quantification

It was stated previously that techniques for OES quantitative bulk analysis are of limited value in depth profile analysis: in spite of this: several authors have demonstrated successful use of such techniques for specific applications. At an early stage, BELLE and JOHNSON [ 2] quantified their results based on calibration curves of high alloy steels similar in composition to their depth profile specimens. In fact they even used a form of sum normalization, and their quantification technique could have been effectively exploited, had it not been for the fact that they worked with photographic detection. In an interesting work, KOCH *et al.* [14] were able to quantify integrated signals by using measurements with alternative analytical methods for calibration. In this way, they achieved the first real "coating weight" measurements with GD-OES. They also demonstrated the simple, but effective, approach to quantification by "extrapolating" signal levels on the surface to the known bulk content of the sample. Quantitative work based on this approach was also published by QUENTMEIER *et al.* [12]. The main drawback with this technique is that it is only applicable to elements which are present in measurable quantities in the bulk. For the problem of determining sputtered depth, the most important early work is that of BOUMANS[13]. He showed that the sputtering rate in a GD can be described by the empirical relation

$$q_b = C_{qb}i(U - U_{0b}) \quad (1)$$

where  $q_b$  is the sputtering rate of sample b;  $i$  is the current;  $U$  is the voltage; and  $C_{qb}$  and  $U_{0b}$  are *sputtering rate constants* characteristic of the sample b.  $C_{qb}$  is related to the sputtering yield (probability of a sputtering event per ion impact) of the material;  $U_{0b}$  is a threshold voltage that, in the Grimm source, is close to 300 V for a large number of materials. Equation (1) shows that the sample loss rate increases linearly with current and voltage, as is illustrated graphically by plotting the reduced sputtering rate  $q_b/i$  vs voltage (see Fig. 3). BOUMANS [13] measured the sputtering rate constants of several pure metals and some alloys. Several other workers [7, 15-18] have measured sputtering rates for the Grimm source; in general, the agreement between independent measurements is very good.

In another paper KOCH *et al.* [17] introduced the concept of "internal quantification" of oxide and nitride layers. By "internal" it is understood that the quantification is based on the measurement of sputtering rates of the pure metals. It is interesting to note that the basic assumption of their method is that the optical emission signal is proportional to the sputtering rate. This assumption is also the basis for the more

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Table 1. Sputtering rates and Ni 231.6 nm emission intensities in two different alloys (excitation condition 60 mA at 700 V)

	Ni concentration (w%)	Sputtering rate ( $\mu\text{g/s}$ )	Emission intensity (arbitrary units)
Copper-nickel	10.8	18.0	22 670
Stainless steel	10.1	7.4	9490

general quantification methods existing today. However, KOCH *et al.* used their method for thickness determinations of oxide and nitride layers only, and did not exploit their idea further [17].

### 3. The Emission Yield Concept

If a CuNi alloy with 10% Ni is measured with a GD-OES instrument, the

measured Ni signal intensity is approximately 2.4 times that of a stainless steel with an equal Ni concentration. measured under identical discharge conditions. Measuring the sputtering rates of the two samples. it is found that the ratio of these matches that of the Ni intensities (see Table 1). Intuitively. this observation is easy to accept: the emission intensity should be proportional to the sample atom density in the plasma. which in turn should be proportional to the sputtering rate. If we allow the voltage. current and pressure to vary. the situation becomes more complex. However, disregarding this complication for the time being, the sputtering rate-intensity proportionality provides for an elegant solution to the quantification problem based on the concept of *emission yield* [19]. 20J, which can be defined as the emitted light per unit sputtered, mass of an element. Mathematically. this leads to the relation:

$$\delta w_n = I_{nm} \delta t / R_{nm} \quad (2)$$

where  $\delta w_n$  is the mass sputtered of element n during time increment  $\delta t$ ;  $I_{nm}$  is the emission intensity of spectral line m of element n;  $R_{nm}$  is the emission yield of spectral line m of element n. which is an atomic- and instrument-dependent quantity.

Equation (2) is equivalent to:

$$I_{nm} = c_n q_b R_{nm} \quad (3)$$

where  $c_n$  is the concentration of element n in sample segment b;  $q_b (= \delta w_n / \delta t)$  is the sputterine rate in sample segment b.

For Eqns (2) and (3) to be generally valid. it is assumed that  $R_{nm}$  is independent of the sample matrix. This has been investigated by several authors [21-23], and is by now widely accepted to be valid, at least to a first approximation.

### **3.1 Quanrification based on the emission yield – development in Japan**

The emission yield concept as a basis for quantification of depth profiles was first proposed by PONS-CORBEAU and others from IRSID in France [19]. However, this concept was first put to effective use for complete quantification (conc vs

depth) by several Japanese workers [21, 24, 25]. It is not clear which author did the original work in Japan. but special credit goes to OHTSUBO and his group for some of the best method development work in this field.

The, method described by OHTSUBO *et al.* is based on Eqn (2), which, in some publications. also includes a background correction term. The *total* sputtered mass  $\delta W_b$  during time increment  $\delta t$ . assuming that all elements of significant concentration are measured. is given by:

$$\delta W_b = \sum_n \delta w_n . \quad (4)$$

It follows that the concentration  $c_n$  (in weight percent) of element  $n$  in the corresponding sputtered segment  $b$  can be expressed as:

$$c_n = (\delta w_n / \delta W_b) 100 . \quad (5)$$

Having obtained the total sputtered mass from Eqn (4). the thickness  $\delta d_b$  of segment  $b$  can be calculated according to:

$$\delta d_b = k \delta W_b / \rho_b \quad (6)$$

where  $k$  is a geometrical conversion factor depending on the anode shape:  $p \sim$  is the density of sample segment  $b$ . The density must be estimated from the concentration.  $c_n$ . In one paper TAKIMOTO *et al.* [21], this is accomplished by summing over the fractional volumes of each element. Mathematically. this can be expressed as:

$$1/\rho_b = \sum_n c_n / (\rho_n 100) \quad (7)$$

where  $\rho_n$  is the density of element  $n$ . Alternative algorithms are possible and will be discussed in a later section of the paper. In Eqn (2), the solution to both the concentration and depth calibration problems are embedded. In several papers describing this method, the determination of the emission yields. which constitutes the calibration of the spectrometer systems. is accomplished by measuring the integrated signals from specially prepared samples with coatings of

known thickness and composition. Quantification according to the above method has been realized in software, which is also commercially available. Spectrometer systems with such software are used extensively in Japan for production control of various coated materials.

### 3.2 The IRSID method

As was stated in the previous section, emission yields as a basis for quantification was originally introduced by PONS-CORBEAU *et al.* [19, 22]. However, in their work they developed an algorithm based on *ratios* of emission yields to that of a major element rather than using absolute values. This approach has the advantage that there is some compensation for variations in the excitation parameters, but it limits the method to quantification of elemental concentrations only since the sputtered mass cannot be determined by means of emission yield ratios. The sputtered depth still had to be determined by means of actual sputtering rate measurements on each sample material studied. In a recent extension of the original IRSID method, depth quantification by means of *absolute* emission yields, similar to the method described by TAKIMOTO *et al.* [21], is included [26]. For calibration it is normally sufficient to determine  $R''$  initially for just *one* element (e.g. the major element of the samples to be analysed) and analytical line by means of a reference sample with a known sputtering rate. Once this is accomplished, *ratios* of emission yields for any other spectral line in the spectrometer system can be determined by means of intensity ratio measurements on other reference materials. Consider simultaneous intensity measurements for several elements on a reference sample. From Eqn (3) it follows that

$$I_{kl}/I_{nm} = c_k R_{kl} / c_n R_{nm} \quad (8)$$

Obviously, if  $c_k$ ,  $c_n$  and  $R_{nm}$  are known,  $R_{kl}$ , can be determined.

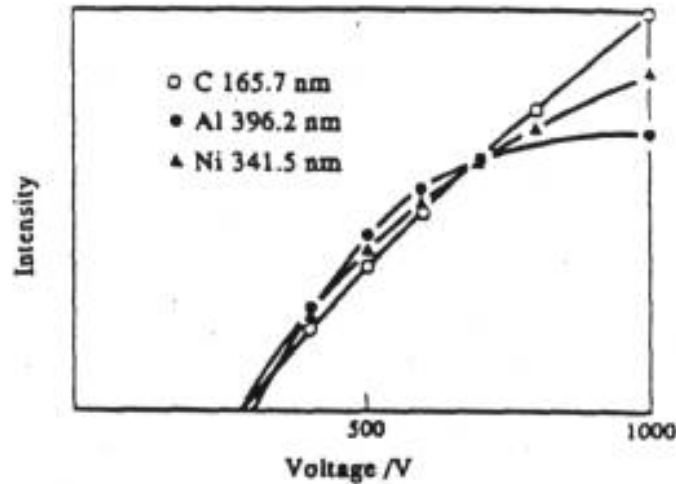


Fig. 4. Emission intensity vs voltage graphs for different spectral lines, recorded at 60 mA: ● Al 396.2 nm; ▲ Ni 341.5 nm; ○ C 165.7 nm.

### 3.3. The empirical intensity expression and the SIMR quantification method

At the Swedish Institute for Metals Research (SIMR), the first work on the quantification problem [18] was not based on the concept of emission yield. Instead, an empirical intensity expression for the GDL was derived based on experimental work. The basic sputtering rate-intensity proportionality was observed at an early stage of the work, but in addition it was deemed necessary to take variations in the excitation parameters (voltage and current) into account. The reason for this is that, in most applications of interest, at least one of the excitation parameters will vary with depth as layers of different composition are penetrated. Furthermore, different applications require different settings of the excitation parameters, and it is of practical value to be able to calibrate for a wide range of applications with one set of calibration constants. By varying the voltage and current systematically, it was found that the intensity increases approximately as the square of the current for several analytical lines of interest. The voltage dependence showed the expected drop towards zero intensity in the vicinity of the threshold voltage for sputtering. Above the threshold voltage the intensity increase was found to be less than linear with the voltage, with a tendency to saturate above 1000 V (see Fig. 4). Based on these observations the following empirical intensity expression for spectral line  $m$  in sample segment  $b$  was proposed [18]:

$$I_{nm} = k_m c_n C_{qb} i^2 (U - U_{0b})^{B_m} \quad (9)$$

where  $k_m$  is an atomic- and instrument-dependent constant characteristic of spectral line  $m$ :  $B_m$  is a matrix-independent constant, characteristic of spectral line  $m$  only. with experimentally derived values in the range 0.2-0.6. In further investigations involving more spectral lines. it was found that Eqn (9). where the intensity increases as the square of the current. is not a generally valid approximation. By replacing the exponent 2 for the current dependence with a variable constant  $A_{nm}$ , a considerably better fit to experimental data was obtained (see Fig. 5). Also, it was found that the exponential function for the voltage dependence in Eqn (9) could more conveniently be replaced by a polynomial. which does not include  $U$  explicitly, An improved empirical intensity expression based on these findings was given [26] as:

$$I_{nm} = k_{nm} c_n C_{qb} i^{A_m} f_m(U) \quad (10)$$

where  $A$  is a matrix-independent constant, characteristic of spectral line  $m$  only:  $f(U)$  is a polynomial of degree 1-3, also characteristic of spectral line  $m$ . The constants  $A_m$  have been experimentally determined for a large number of spectral lines: several examples are given in Table 2. Numerically.  $A$  varies between 1.0 and  $Z.S.$  but a remarkably large proportion of the measured values are relatively close to 2. in accordance with the original Eqn (9).

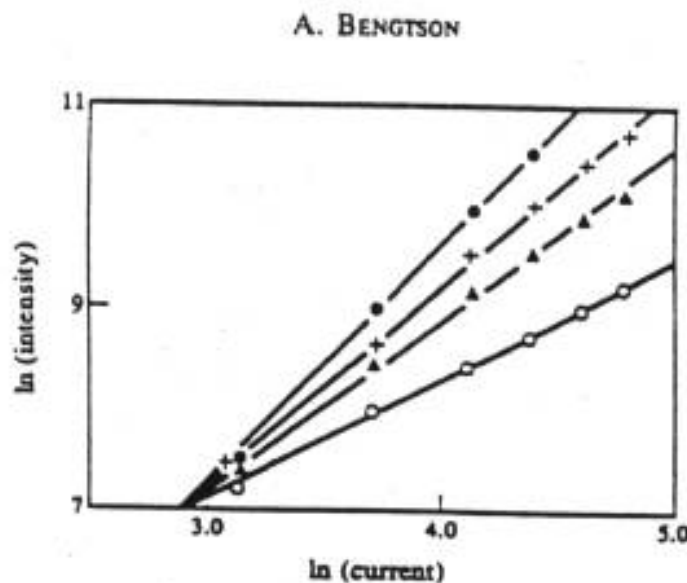


Fig. 5. Log-log graphs of emission intensity vs current for different spectral lines, recorded at 600 V: ● Al 396.2 nm; + Si 288.2 nm; ▲ Ni 341.5 nm; ○ C 165.7 nm.

Using "hand-waving" arguments, the fact that the intensity nearly depends as the

square of the current can perhaps be qualitatively understood in the following way. As shown by BOUMANS [13] the sputtering rate, and thereby the sample atom density in the plasma, increases linearly with the current. The current density, and thereby the number of charged particles in the plasma, is also expected to increase linearly with the current. The last assumption is based on the fact that the power density in a glow discharge is rather low, and non-linear phenomena are therefore unlikely to be predominant. Since the major excitation mechanisms involve collisions with charged particles, the two effects combined should give the observed near-square current dependence.

The observed effect of voltage on intensity is more difficult to interpret in qualitative terms. The sputtering rate increases linearly with voltage [13] as does the average kinetic energy of the charged particles. By analogy with the arguments for the intensity dependence of the current, one would expect a near-quadratic intensity increase with voltage as well. The observed functional intensity dependence on voltage is in fact more close to square-root for most spectral lines, with a tendency to saturate above 1000 V as was mentioned earlier. One of several reasons for this could be that an

Table 2. Constants  $A_m$  for the exponential current dependence of spectral line intensities. Averages of measurements performed at 600 and 900 V

Element	$\lambda$ (nm)	$A_m$	Materials used
C	165.7	$1.2 \pm 0.1$	Steel, cast iron, tungsten carbide
P	178.2	$1.6 \pm 0.1$	Steel, cast iron
S	180.7	$1.4 \pm 0.1$	Steel, cast iron
Fe	271.4	$1.8 \pm 0.2$	Steel, brass
Si	288.2	$2.0 \pm 0.2$	Steel, brass, aluminium
Ni	341.5	$1.6 \pm 0.1$	Steel, brass, aluminium
Mo	386.4	$2.2 \pm 0.2$	Steel, cast iron
Al	396.2	$2.1 \pm 2$	Steel, brass
Mn	403.4	$2.0 \pm 0.2$	Steel, cast iron, brass
Cr	425.4	$2.3 \pm 0.2$	Steel, cast iron, aluminium
Cu	327.4	$2.2 \pm 0.2$	Steel, aluminium
Cu	296.1	$1.4 \pm 0.2$	Brass, copper
Zn	334.5	$2.1 \pm 0.2$	Brass, aluminium
Pb	405.8	$2.2 \pm 0.2$	Brass
N	174.3	$1.4 \pm 0.2$	Hard metal (coronite)
O	777.7	$1.1 \pm 0.2$	Conducting ceramic

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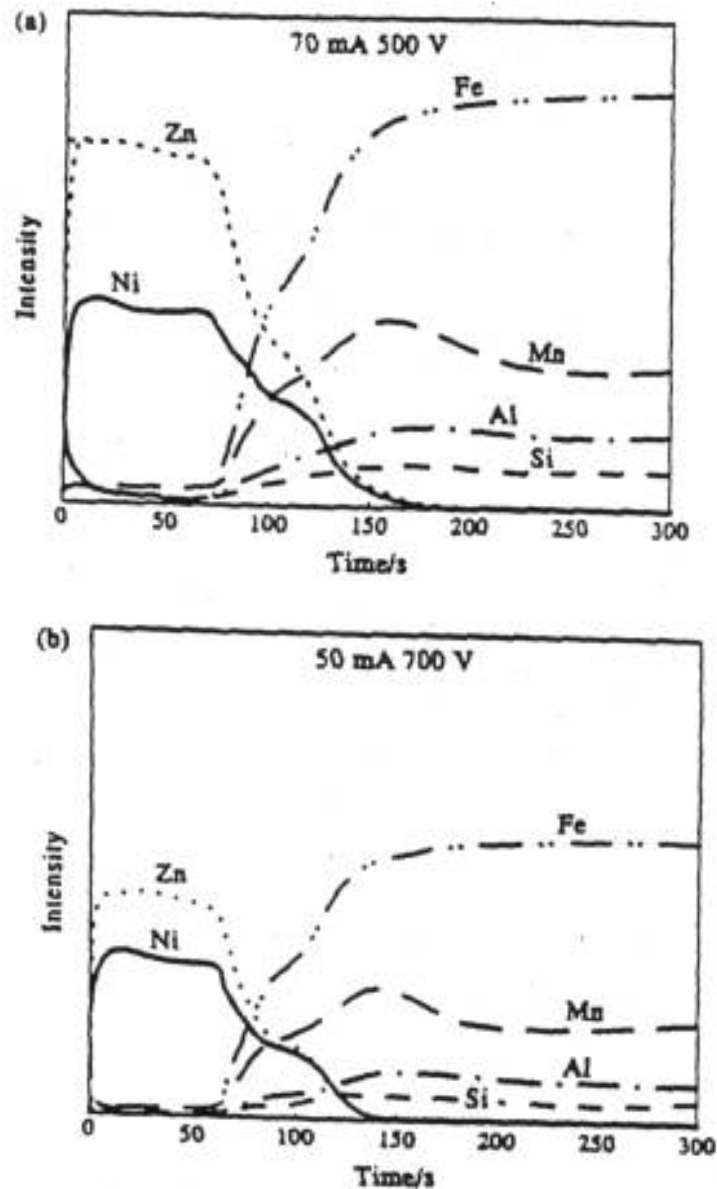


Fig. 6. Intensity vs time depth profiles of a ZnNi electroplated steel, recorded at two different settings of the excitation parameters.

increase in voltage is effected by decreasing the pressure in the source. This also has the effect that the cathodic dark space (the distance between the sample surface and the negative glow) increases [15]. Since the transport of sputtered atoms to the negative glow is a diffusion process, the sample atom density falls exponentially with the distance from the sample surface. The increased length of the dark space therefore has the additional effect that a smaller percentage of the sputtered atoms will reach the negative glow and contribute to the optical emission. For current, the opposite effect occurs, perhaps explaining why  $A_m$  constants greater than 2 are observed. There are also experimental observations reported [27] indicating that the electric field itself counteracts the diffusion process. This would change the diffusion profile so as to further decrease the sample atom density in the negative glow.

It is not suggested that the arguments given above offer any deeper understanding of the

complex physics of glow discharges. Such in-depth studies are found in Refs [15, 28, 29]. However, it is clear that much more work is needed if we want to achieve a better understanding of glow discharges on the fundamental level. The emission yield varies with the excitation parameters  $f_2I$ ,  $27J$  which is well illustrated by the depth profiles of an electroplated ZnNi layer in Fig. 6. The empirical intensity expression gives the possibility to correct for these variations. Combining Eqns (1), (3) and (10), the following expression for  $R_{nm}$  is obtained:

$$R_{nm} = k_{nm} i^{(\lambda_m - 1)} f_m(U) / (U - U_{0m}) . \quad (11)$$

By incorporating Eqn (11) into one of the emission yield quantification methods, the desired compensation for variations in the excitation parameters can be achieved. However, this particular approach has not been adopted in the SIMR quantification method, which will be outlined in more detail in the following sections. In any glow discharge, the plasma conditions are determined by three physical parameters: pressure, voltage and current. These three parameters are not independent: if any two of them are fixed the third is determined by the sample material. In the work at SIMR leading to the empirical description of intensity variations it was assumed that the pressure, which is not included explicitly in Eqn (10), has little influence on the emission yield. In a recent paper PAYLING and JONES [30] argue that the pressure actually is the *only* physical parameter with a significant influence on the emission yield, and the voltage-current intensity dependence found in Eqn (10) largely reflects variations in the emission yield due to pressure. Experimental evidence in support of this view is also given. It can be shown that for several applications involving small pressure variations, both the SIMR model and that of Ref. [30] will give very similar quantitative results. However, accurate quantitative results have also been obtained by means of Eqn (10), and one set of calibration data for both Fe- based and Al-based samples [31] (two materials that have to be measured at substantially different pressure settings). These results are very hard to explain by means of PAYLING'S approach. Resorting to more "hand-waving" arguments, it is also difficult to see how the emission yield, which in part is a measure of the excitation probability of analyte atoms, could *not* be affected by current and voltage. Work is in progress in order to further investigate the relative influence of voltage, current and pressure on the emission yield.

### 3.3.1 Sputtering rare normalization and measured intensities.

One of the main objectives in the SIMR quantification project was to devise a calibration procedure, which as closely as possible resembles that of standard bulk analytical techniques. That is for each element, a concentration vs intensity function is established based on intensity measurements on bulk reference materials of known composition. The main difference compared with standard calibration procedures for bulk analysis is that it is necessary to use reference materials of widely different compositions, due to the previously mentioned multi-matrix character of depth profile analysis.

The first step in the SIMR calibration procedure is to select a *reference excitation condition*. For the 8 mm lamp, 60 mA at 700 V is normally selected. The second step is to select a *reference matrix* (material type) with a well-known sputtering rate. At SIMR, low-alloy steel is used for this purpose due to the abundance of such reference materials and the fact that the sputtering rate of steel is about mid-range compared to several other matrices. Intensity measurements on the selected calibration samples are performed at the reference excitation condition for all samples. In practice, this means that the gas flow (or pressure) in the source has to be adjusted for the different types of materials. In several modern spectrometer systems this can be achieved automatically by means of a mass flow controller. In the concentration vs intensity diagrams, the as-measured intensities normally show considerable scatter (see Fig. 7(a)). This is an inevitable result of the differences in sputtering rates, as shown in Eqn (3). In order to compensate for this effect, the measured intensities are *normalized* to the sputtering rate of the reference matrix. This is done by multiplying the measured intensities of each calibration sample with a factor, equal to the ratio of the sputtering rate of the reference matrix to that of the, sample itself. Mathematically this is given by:

$$I_{nm}(\text{normalized}) = I_{nm} q_{ref} / q_s \quad (12)$$

where  $q_{ref}$  and  $q_s$  are the sputtering rates of the reference matrix and the calibration sample s, respectively. Obviously, the sputtering rates of the calibration samples used must be known. The result of the sputtering rate normalization is exemplified in Fig. 7(b) where Zn intensities from pure Zn, brasses, and some AlZn alloys are located along a straight line.

The calibration procedure described above has several practical and analytical advantages. Only bulk materials are necessary for a complete calibration rendering the specially produced coated reference materials unnecessary. A large

number of bulk reference materials are available at a reasonable cost. Another advantage with the use of these is the large number of elements that are certified and thereby quantifiable. As an example of how the sputtering rate-normalized calibration is utilized for a concentration vs depth quantification, consider a brass sample that is measured as an unknown. It can be inferred (see Fig. 7(a) where the solid line indicates the slope of the normalized calibration curve) that the measured Zn concentration will be some 4.5 times higher than the correct value. If Eqns (2) and (3) are correct, this must be true for all other elements in the sample as well, and the sum of concentrations of all elements will be approximately 450%. A sum normalization to 100% gives the correct elemental concentrations: in addition the sputtering rate is obtained as 4.5 times that of the reference matrix. In principle, samples of any composition can be measured in this way, provided that there is calibration data for all major elements in the sample. Up to this point, the SIMR quantification method is essentially equivalent to the emission yield technique utilized by Japanese authors and at IRSID. In all three methods, there is a sum normalization performed, and the effective sputtering rate is determined by summing over the emission intensities from all major elements in the sample.

### **3.3.2. Intensity normalization to the reference excitation condition.**

As was explained in the previous section, the SIMR quantification method is based on a calibration performed at pre-determined levels of voltage and current (the reference excitation condition). In order to allow measurements to be taken at other excitation conditions, the first calculation step in the evaluation procedure is to *normalize the measured intensities* to the reference excitation condition. This is accomplished with the empirical intensity expression, Eqn (10), with constants adjusted to yield the numerical value 1.0 at the reference point. A set of 3-5 constants for each spectral line ( $A_m$ ,  $f_m$  (U)) are needed: these are collected together with atomic data for the elements in a reference library. Using the normalized intensities, evaluation of the concentrations proceeds according to the technique described in the previous section.

### **3.3.3. Calculation of the sputtering rate using Boumans equation.**

In the evaluation of the sputtering rate, it is also necessary to take variations in voltage and current into account. This is done by using Boumans' equation (1) to calculate, for each segment of the depth profile, the sputtering rate of the *reference matrix*. In this calculation, the actual (measured) values of voltage and current are used. This calculated value of the reference matrix sputtering rate is multiplied by the sum normalization factor described in Section 3.3.1 yielding the effective sputtering rate of the corresponding segment of the depth profile.

### 3.3.3 Use of an Ar emission line as an internal standard.

As was stated earlier, 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 carrier gas used) is always present as the major element in the plasma. In software based on the SIMR quantification method, it is possible to use an Ar spectral channel as internal standard. The empirical intensity expression remains valid and it is only necessary to adjust the line-dependent constants accordingly. The idea of using Ar as an internal standard dates back to the original work on the empirical intensity expression [18], where it was found that Ar and analytical spectral lines generally show very similar response to voltage variations. Consequently, by ratioing analytical line intensities with an Ar channel, the voltage intensity dependence is nearly eliminated. The intensity dependence on current is also reduced as well as some of the low-frequency flicker noise present in a glow discharge. The expected analytical advantages would therefore improve the accuracy and precision of the elemental determinations.

The use of an Ar line as internal standard is only meaningful if the Ar emission intensity is independent of the sample matrix at constant excitation conditions. Experimentally this has been found to be true only in the first approximation, or within 15% relative to an average intensity value. The variations observed are large enough that the depth calibration accuracy could be affected. On the other hand, it is possible that the matrix-dependent variations in the Ar emission intensity are proportional to the *excitation probability* for analyte atoms. If that is the case ratioing with an Ar line should compensate for such variations, actually improving the depth calibration accuracy. Furthermore, there is a possibility that some compensation for the matrix-dependent variations in the sputtering rate threshold voltage,  $U_0$ , is achieved by this technique. These and other questions concerning the merits of using an Ar internal standard remain to be experimentally investigated.

### 3.4 Quantitative depth profile analysis with GD-MS

In recent years, GD-MS has emerged as an interesting alternative to GD-OES for rapid, multielement depth profile analysis. The MS technique has two major advantages over OES – generally lower detection limits and a more complete elemental coverage. For GD-MS, the methods for quantitative evaluation of depth profiles are not yet as developed as those for GD-OES. In a few reported quantitative applications, use is made of standard techniques for quantitative bulk analysis, combined with a depth calibration based on sputtering rate measurements of the particular materials investigated [32]. This approach works well for specific applications but is too limited to be considered as an effective solution to the quantification of depth profiles. Standard GD-MS techniques for quantitative analysis are based on the use of relative sensitivity factors (RSF) related to an internal standard or reference element.

#### Review: Quantitative depth profile analysis

Table 3. Analytical figures of merit for glow discharge spectrometry

Figure of merit	OES	MS
Lower limit of detection (ppm)	1–100	0.01–10
Minimum detectable number of atoms (atoms/cm <sup>2</sup> )	10 <sup>13</sup> –10 <sup>15</sup>	10 <sup>11</sup> –10 <sup>14</sup>
Minimum information depth	1 nm	1 nm
Relative instrumental depth resolution	10%	10%
Penetration rate	1–100 nm/s	0.1–10 nm/s
Short term precision (major and minor elements)	<1% RSD	1–5% RSD

In a general approach to quantitative depth profile analysis, such techniques cannot be applied (see Section 2). JAKUBOWSKI and STEUWER [4] have suggested an alternative method based on absolute sensitivity factors. At constant discharge voltage, these factors are defined as

$$S_n = I_n^+ / (ic_n Y_1) \quad (13)$$

where  $S_n$  is the absolute sensitivity of element n:  $I_n^+$  is the ion current for

element  $n$ ;  $i$  is the discharge current;  $c_n$  is the concentration of element  $n$ : and  $Y_t$  is the total sputtering yield of the sample.

Since the product  $iY_t$  equals the total sputtering rate of the sample, Eqn (13) is the MS equivalent of Eqn (3) for OES, with  $S_n$  replacing the emission yield  $R_{nm}$ . It would therefore appear that essentially the same quantification techniques can be applied for GD-MS as for GD-OES. JAKUBOWSKI and STEUWER [4] have also demonstrated several successful applications of Eqn (13) for quantification of depth profiles. However, JAKUBOWSKI also expresses considerable caution concerning the general applicability of this technique. One of the problems is that the absolute sensitivity factors depend on the selected operational parameters of both the GD and the mass spectrometer itself. Clearly, more work is needed before it can be concluded that the use of absolute sensitivity factors is the key to a more generally applicable quantification method for GD-MS. Until this can be established, or some alternative, general solution to the quantification problem is devised, GD-OES remains a more versatile technique for quantitative depth profile analysis than GD-MS.

### ***3.5 Analytical figures of merit for glow discharge spectrometry***

For any instrumental technique, the analytical figures of merit varies considerably, depending on the application and the type of instrument used. Furthermore, technical development tends to improve the performance of instruments, rendering published data obsolete very quickly. With these facts to be considered, some analytical figures of merit for state-of-the-art glow discharge spectrometry are given in Table 3. A further comment on the data presented here is that the lower limit of detection normally cannot be attained at the minimum information depth.

### ***3.6 Applications of quantitative depth profile analysis***

The number of documented applications of quantitative depth profile analysis by glow discharge is rather large, and rapidly increasing. Metal coatings of various types make up the majority of the published applications, but the technique has also been successfully applied to oxides, nitrides, and several other non-metal coatings.

## A. BENGTON

Table 4. Selected applications of quantitative depth profile analysis by glow discharge

Material type	Analytical problem	References	Figures
Electroplated steels	Coating thickness, composition of major elements	21, 22, 24, 25, 27	8
Hot dipped galvanized steels	Coating thickness, distribution of alloying elements in coating/interface, surface treatments	18	9, 10
Cold rolled steels	Surface enrichment/depletion of minors and traces, surface contamination	12, 14, 22	
Hot rolled low-alloy steels	Oxide thickness, enrichment/depletion of minors and traces in interface	31	11
Hot rolled high-alloy steels	Oxide thickness and composition, enrichment/depletion of major elements	23	
Nitrocarburized steels	Thickness and composition of heat treated zone, distribution of N and C in different phases	35	
High temperature nitrided titanium alloys	Thickness and composition of compound layers, segregation of alloying elements	36	
PVD-coatings of TiN, TiCN, CrN etc.	Thickness and stoichiometry of coatings, check of unwanted contaminations	37	12
Phosphated steels	Thickness and composition of phosphate layer	20	
Tribochemical layers on metals	Thickness and composition of layer, diffusion of matrix elements	38	
TiH on titanium metal	Thickness and composition of TiH layer	39	

In order to make a comprehensive presentation of the rather numerous reported applications, a list with brief descriptions of some general types is given in Table 4. This list is far from complete, but it gives some idea of the considerable versatility of glow discharge spectrometry. A few of the application types are illustrated by figures, and discussed in somewhat more detail below.

### 3.6.1 Electroplated steels.

Owing to its excellent corrosion resistance, electroplated sheet steel is used extensively in the automotive industry. The plating material is typically Zn or some Zn alloy with a coating thickness of typically 5-10  $\mu\text{m}$ . The coatings are normally very homogeneous, both with respect to thickness and composition. One of the most common alloy types is ZnNi (see Fig. 8). The major analytical problem is to determine the thickness, or coating weight, and the Ni content. Surface contamination may also be of interest; in particular contamination on the original steel surface, appearing as enrichments in the Zn/Fe interface.

### **3.6.2 Hot dipped galvanized steels.**

Hot dipped sheet steel represents a perhaps less advanced production technology than electroplating, but as an analytical problem it is more demanding. Compared to electroplated material, hot dipped Zn coatings have a considerably more complex metallurgical structure. In many of these materials, the analytically most interesting feature is a thin interface layer consisting of FeAl phases (see Fig. 9). In a GD depth profile, the profiles at this interface are broadened by the limitation in depth resolution caused by the non-flat bottom of the sputtering crater (see Fig. 2). In addition, the profile shape is more or less distorted by differential sputtering processes linked to the metallurgical structure. Not uncommon, these effects lead to the appearance of multiple Al peaks in the interface. The integrated quantity of Al in the interface can be accurately determined but the mechanisms responsible for the more detailed shape of the depth profile in the interface are not well understood.

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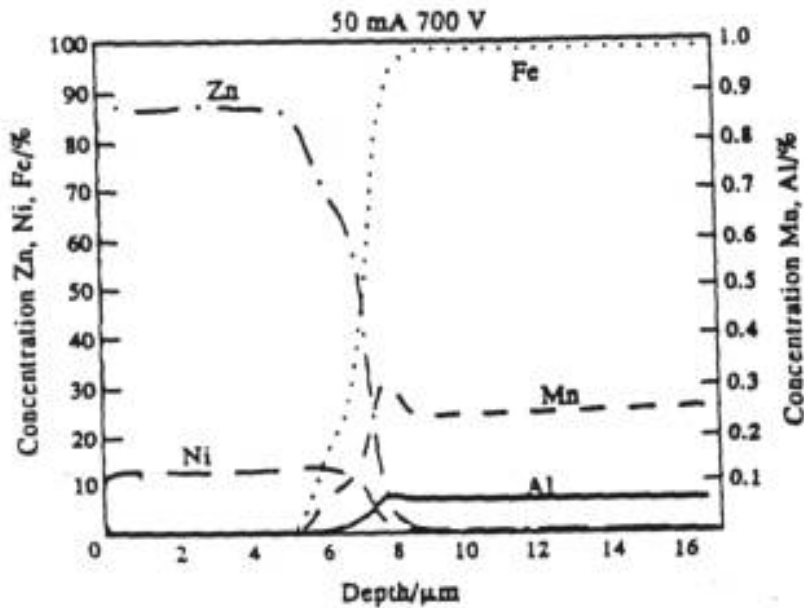


Fig. 8. Quantitative depth profile of ZnNi electroplated steel.

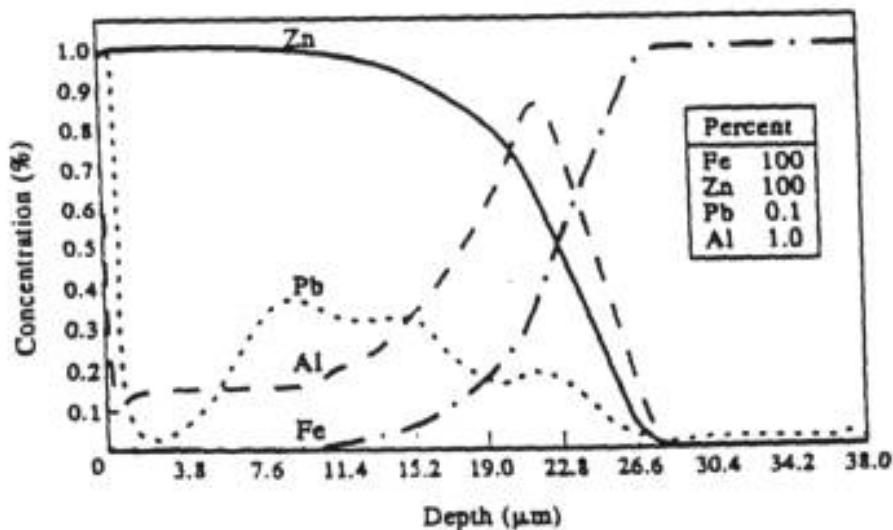


Fig. 9. Quantitative depth profile of hot dipped galvanized steel.

For hot dipped material the top surface ( $< 1 \mu\text{m}$ ) layer is often of considerable analytical importance. Substantial enrichment of Al and Pb is typically present. Other technical reasons to study the top surface may be additional surface treatments, e.g. chromatization. In Fig. 10. the first 100 nm of the depth profile from Fig. 9 is shown,

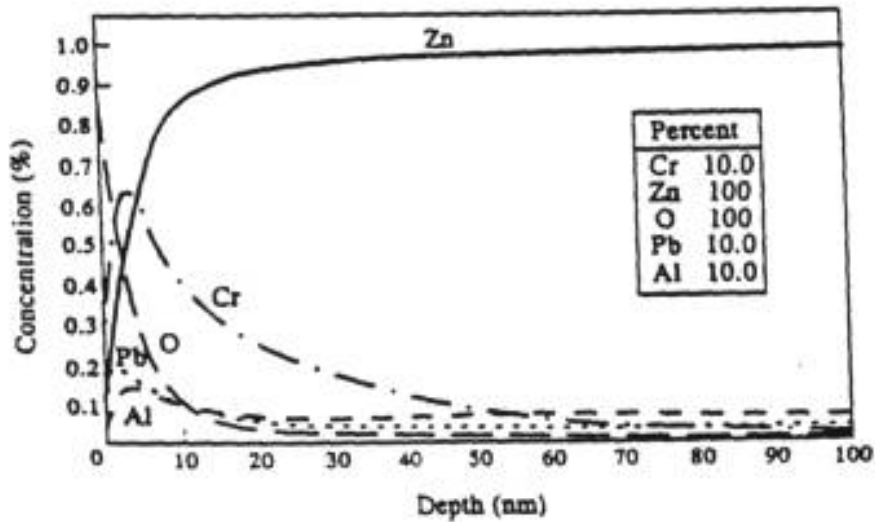


Fig. 10. Quantitative depth profile of chromate layer on hot dipped galvanized steel.

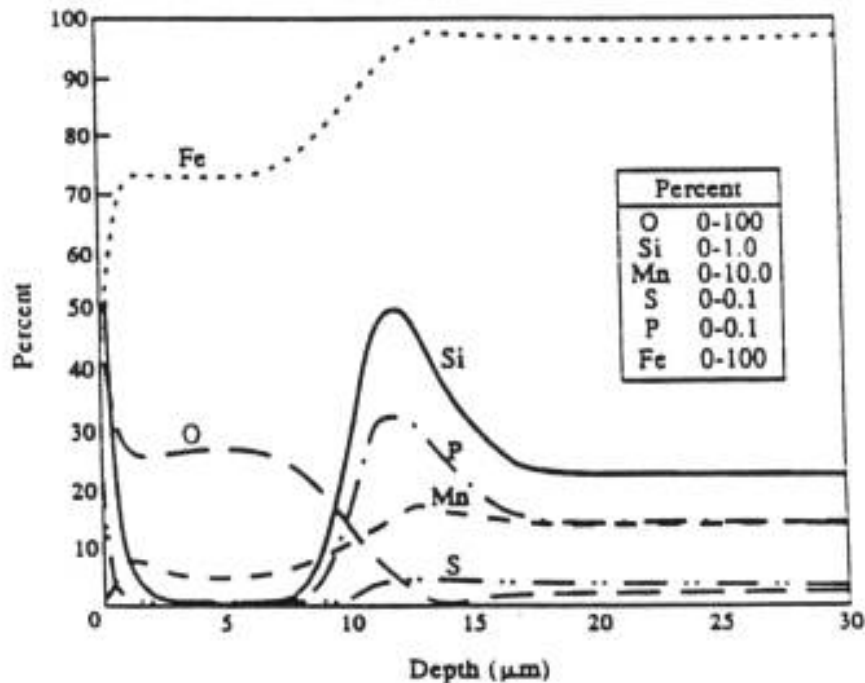


Fig. 11. Quantitative depth profile of hot rolled low-alloy steel.

revealing a thin chromate layer. This example illustrates both the capability of GD spectrometry to profile rather thin ( $< 100$  nm) layers, as well as the large dynamic range in depth which is obtained in a single measurement.

### 3.6.3 Hot rolled steels.

Hot rolled low-alloy steels were among the first applications of GD-OES for depth profile analysis in the steel industry. The oxide thickness and elemental segregation in the oxide/steel interface is of importance for the control of the pickling process (see Fig. 11). The quantitative depth profile shows that Si and P

have segregated to the interface. while Mn more or less follows the Fe concentration profile. For hot rolled high-alloy steels. the major analytical problem often concerns the Cr-depleted zone underneath the oxide scale. resulting from selective oxidation of Cr. With quantitative GD depth profile analysis. it is possible to rapidly determine to what depth the material must be pickled in order to reach a specified Cr content on the surface.

### **3.6.4. TiN and other non-metallic coatings on hard materials.**

Physical vapour deposition (PVD) and chemical vapour deposition (CVD) type coatings are becoming increasingly important analytical applications for quantitative GD depth profile analysis. TiN. TiCN. CrN and other nitridic compounds are commonly used in order to increase the wear resistance of cutting tools. The processes used to produce these coatings are complex. and there is a need for analytical techniques that can be used to control the coatings on a routine basis. In Fig. 12 an example of an essentially stoichiometric TiN layer on tungsten carbide is shown. A carbon peak at a depth of 3-4  $\mu\text{m}$  is evidence of the fact that the PVD process has been disturbed at some point. so as to produce a localized carbon contamination of the TiN layer.

## **4. Limitation of current Quantification Methods**

In this paper, the evolution of quantitative depth profile analysis by glow discharge into a firmly established and highly successful analytical technique has been presented. The quantification techniques in existence have been shown to give accurate results for a large variety of applications. This has indeed been a very satisfying development. but there are still several problems remaining which need to be addressed in forthcoming research. Some of these problems are discussed below.

## Review: Quantitative depth profile analysis

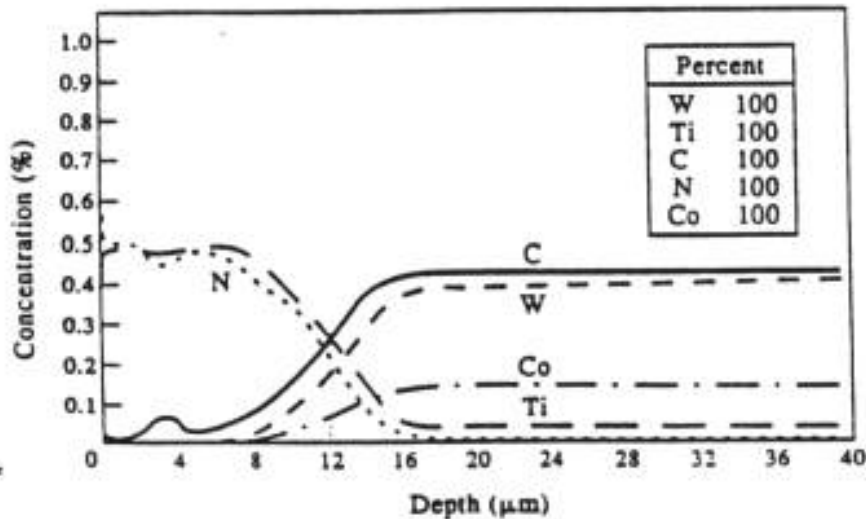


Fig. 12. Quantitative depth profile of TiN layer on tungsten carbide. concentrations in atom percent.

## 4.1 Reference materials for calibration

Glow discharge spectrometry, being an instrumental technique for direct solids analysis, has to rely on reference materials for calibration. For accurate determinations, a calibration based on Certified Reference Materials (CRM) is desirable. A large number of CRMs, used for bulk analysis of metals and alloys is available for this purpose. However, for some elements, there are very few or simply no CRMs at all available. In particular, CRMs with high concentrations of the gaseous elements O, N and H are lacking. For these elements, various non-certified reference materials are currently in use, and some of these may give inaccurate results. Clearly, this is not a satisfactory situation and work is in progress to find suitable materials that may serve as CRMs for the gaseous elements in the future. Further types of CRMs required are coated samples with a certified thickness and coating composition. There are such materials commercially available, but very few are properly certified. Although not strictly necessary for calibration purposes, these materials are valuable in order to verify that the calibration of a depth profiling instrument is accurate.

## 4.2 Accuracy of the depth determination

In most quantification methods in use today, the sputtering rate in terms of mass loss is continually measured by means of the sum of intensities of the analytical signals. As was discussed in Section 2.3, this is the most general approach to the depth determination problem which has been devised to date. However, in order to transform mass into depth, the density of the material must be known. The only basis for an estimate of the density is the elemental composition, since there is no additional analytical information available. One approach to this problem is to simply take a weighted average of the densities of the pure elements, according to their concentrations in weight percent [24]. This method gives reasonably accurate results, provided that the major elements have similar atomic masses (e.g. ZnFe, ZnNi, CuZn, FeCrNi). A somewhat more advanced method, which is the one adopted by SIMR, is to calculate a weighted average according to the concentrations in atom percent. This method is essentially based on the assumption that all atoms, regardless of the atomic mass, occupy the same volume in a solid. With the exception of a few unusually large atoms, this is a reasonable first-order approximation. The calculation algorithm utilized by TAKIMOTO *et al.*, summing over the fractional volumes of each pure element (see Section 3.1) [21], is functionally almost equivalent to the SIMR method. These two methods give very accurate results for all metal alloys, including those consisting of elements with significantly different atomic masses, for example AlZn and SnPb. Significant uncertainties in the estimate of the density may occur for more complex materials with gases and other light elements as major constituents, for example oxides, nitrides and carbides. Firstly, there is the problem of CRMs for accurate calibration of elemental concentrations discussed in the previous section. Secondly, the algorithms used for density calculations require that fixed densities be assigned to the pure gases in solid form. It is well known that the volume occupied by, e.g. oxygen atoms, in different metal oxides varies considerably due to the differences in the electronic and lattice structures of the oxides. The densities assigned to the light elements have to be taken as averages, based on measured densities of several materials. Fitted to the SIMR calculation model, these densities turn out to be surprisingly high – 4.2 g/m<sup>3</sup> for O and 4.7 g/m<sup>3</sup> for N. The calculated densities for oxides, nitrides etc. are generally accurate to within 10% but deviations up to 30% have been observed. An inaccurate density will translate into a corresponding systematic error in the determined sputtering depth.

In order to improve the accuracy of the determination of sputtered depth of complex materials, it would be desirable to have a more advanced physical model,

defining the algorithms for the density calculation. However, the lack of phase information about the solid in the GD signals severely limits the possibilities to develop such models. A practical approach, although in many ways unsatisfactory, is to assign variable densities to the gases, thus creating optimized calibrations for specific materials.

### ***4.3 Influence of released molecular species on the emission intensities***

One of several prerequisites for the quantification methods described here to be valid, is that the GD plasma is not affected by chemical reactions involving atomic and molecular species released from the sample. This is true if the sputtered sample atoms make up an insignificant fraction of the plasma gas. In a Grimm-type GD, with a comparatively high sputtering rate, this assumption may not be entirely justified. In the vicinity of the sample surface, the relative content of sputtered material can probably reach percent levels. If the sample contains highly reactive elements (oxygen, nitrogen etc.), it is feasible that a significant fraction of the sputtered material forms molecular species in the plasma. This would lead to a change of signal intensity for certain elements, which cannot be accounted for in the present quantification methods. In a recent paper by FISCHER *et al.* [33], effects of this kind have been observed when the oxygen or nitrogen content in the plasma exceeds a critical threshold of approximately 0.1 mass percent. Since accurate quantification of oxides and nitrides has been demonstrated by several workers, it must be concluded that the critical threshold of gas content is not reached under all sputtering conditions for such materials. However, the problem cannot be dismissed as unimportant, and further investigation is needed.

### ***4.4 Corrections for background and line interferences***

In this paper, background correction of analytical signals has not been included in the general descriptions of quantification techniques. However, background signals do exist in GD spectrometry, and must be correctly subtracted if elements in low concentrations are to be determined accurately. For this particular aspect of

calibration, the multi-matrix character of depth profile analysis introduces some difficulties. It is well known from bulk analysis, that the background signal (often conveniently expressed as a background equivalent concentration, BEC) varies with the sample matrix. If the BEC is made up of an interfering signal from the matrix element, or just plain background noise, it is of no consequence in the evaluation of the concentration, as long as the matrix does not change. In depth profile analysis, the matrix element(s) may change completely as different layers are penetrated, and consequently the BEC will normally change as well. Ideally, a "matrix-independent" BEC should be determined, and all additional contributions to the background treated as element-specific interferences [34]. In practice, it is very difficult to determine the "matrix-independent" BEC from the available calibration data. Also, the compensation for variations in excitation parameters become considerably more involved for signals close to the background level [34]. Undoubtedly, improved techniques for accurate background correction are needed in order to realize the potential for trace analysis in GD depth profile analysis.

*Acknowledgements*—The author is indebted to K. OGLE, H. HOCQUAUX, N. JAKUBOWSKI, W. FISCHER, M. ANALYTIS and R. PAYLING for valuable discussions. This work has been financially supported by the Swedish Board for Technical Development (NUTEK) and Swedish Steel, Copper and Aluminium Industry.

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