Glow discharge optical emission spectrometry for the analysis of metallic coatings on steel

GAMeS

Wetenschappelijk ondersteuningsprogramma voor de normalisatie en technische regelgeving

Eindverslag

N° NM/67/21
NM/G5/22

Federaal Wetenschapsbeleid

Stefan KUYPERS, Hong CHEN, Danny HAVERMANS, Raymond KEMPS,
Michel SCHOETERS & Wolter WEGENER

Yann BOURGEOIS, Karl CRENER & Alain JADIN

VITO – MATERIALS TECHNOLOGY CENTRE
Boeretang 200
B-2400 MOL

CERTECH
Zone Industrielle C
B-7180 SENEFFE

TABLE OF CONTENTS

SUMMARY

A. Context

A method for the determination of thickness and composition of zinc-based coatings on steel was developed in the framework of a standardization project financed by the Belgian federal government. The method is based on radiofrequency glow discharge optical emission spectrometry (RF GD-OES) and uses commercially available instrumentation, software and reference materials.

B. Objectives

The objectives of the project GAMeS were 1) to develop and apply an experimental method, based on RF GD-OES, to determine composition and thickness of zinc-based coatings on steel; 2) to recognize and describe critical factors in the analysis that could prevent both DC and RF GD-OES from becoming a routine tool in the steel industry for the envisaged application; 3) to link up Belgium with the rest of the world as far as GD is concerned.

The research work covered the following aspects: selection of test samples, selection of analytes and their concentration ranges, selection of suitable spectral lines for the different analytes, optimization of analysis parameters, selection and procurement of suitable calibration samples, measurement of densities and sputtering rates of calibration samples, limited interlaboratory exercise on relative sputtering rates, setting up of calibration curves, measurement of compositional depth profiles, determining thickness and composition, interlaboratory comparison on thickness and composition.

C. Conclusions

Analysis results obtained on industrial galvanized and galvannealed test samples with the experimental procedure described in this report are satisfactory and in good agreement with the generally accepted values from ICP-spectrometry. The calibration curves can still be improved by applying a dc bias voltage correction. The interlaboratory comparisons show that 1) relative sputtering rates are not necessarily universal values that can be tabulated and exchanged among users; 2) there is a need for better agreements on how to derive

sputtering rates from profilometer data; 3) the scatter on thickness and composition is too large; 4) GD-OES has not reached the level of a sufficiently accurate routine tool for the analysis of zinc-based coatings.

D. Contribution of the project in a context of support to the processes of standardisation and technical regulations

a) An experimental procedure complementary to the ISO-standard under preparation, which can assist the implementation of this standard. The procedure will be distributed through this report and through a Vito-report based on this report.

b) Experience with the application of RF GD-OES for determining thickness and composition of zinc-based coatings on steel. Expertise and instrumentation of Certech and Vito are available to third parties, for contract work.

c) Awareness of the need for a procedure for measuring crater depths with a profilometer. Even the best standard for GD does not make any sense when crater depths and hence values for the relative sputtering rates cannot be measured correctly. Our results were presented at a meeting of Jobin-Yvon GD users, in the presence of an international expert and member of the ISO/TC201.

d) Awareness of the fact that a relative sputtering rate of a calibration sample can vary significantly and that these variations are not only due to errors in measuring the crater depth. The data were discussed with an international expert in the field and with a Belgian industrial GD user. The results were also presented at a meeting of Jobin-Yvon GD users. More work will be done to substantiate and publish the findings briefly discussed in this report.

e) Awareness of the fact that many European labs are interested to apply or are already applying GD-OES to zinc-based coatings on steel, but that problems exist on the level of calibration, as well as on the level of integration of the compositional profiles. The results of our interlaboratory comparison will be reported to all participants and discussed with active members of the ISO/TC 201.

E. Keywords

GD-OES; glow discharge; spectrometry; standardization; coating; zinc; steel

SAMENVATTING

A. Context

Een methode voor de bepaling van de dikte en de samenstelling van zink-gebaseerde deklagen op staal werd ontwikkeld in het kader van een normalisatieproject gefinancierd door de Belgische federale overheid. De methode is gebaseerd op radiofrequente-gloei-ontlading-optische-emissie-spectrometrie (RF GD-OES) en maakt gebruik van commercieel beschikbare apparatuur, software en referentiematerialen.

B. Doelstellingen

De doelstellingen van het project GAMeS waren 1) ontwikkelen en toepassen van een methode, gebaseerd op RF GD-OES, voor de bepaling van samenstelling en dikte van zink-rijke lagen op staal; 2) (h)erkennen en beschrijven van kritische factoren die zowel voor DC, als voor RF GD-OES hinderpalen kunnen zijn voor het uitgroeien tot volwaardige analysetechnieken voor de beoogde toepassing; 3) België op het gebied van GD laten meespelen op internationaal vlak.

In het onderzoek kwamen achtereenvolgens de volgende aspecten aan bod: keuze van testmonsters, vastleggen van de te analyseren elementen en hun concentratiebereik, keuze van de meest geschikte spectrale lijnen voor deze elementen, optimaliseren van de analyseparameters, selecteren en verwerven van geschikte kalibratiemonsters, het meten van dichtheid en sputtersnelheid van kalibratiemonsters, beperkte interlaboratoriumvergelijking rond relatieve sputtersnelheden, het opzetten van kalibratiecurves, het meten van kwantitatieve diepteprofielen, het bepalen van dikte en samenstelling, interlaboratoriumvergelijking rond dikte en samenstelling.

C. Besluiten

De analyseresultaten die werden bekomen op een reeks van industriële gegalvaniseerde en “gegalvannealde” testmonsters, gebruik makend van de experimentele procedure beschreven in dit rapport, zijn bevredigend en in goede overeenstemming met algemeen aanvaarde ICP-resultaten. De calibratiecurves kunnen nog verder worden geoptimaliseerd

door het toepassen van de zogenaamde dc-biasspanningscorrectie”. De interlaboratorariumvergelijkingen geven aan dat 1) relatieve sputtersnelheden geen universele waarden zijn die men zonder meer kan tabelleren en uitwisselen; 2) er nood is aan goede internationale afspraken voor het bepalen van sputtersnelheden m.b.v. profilometrie; 3) de spreiding op resultaten voor dikte en samenstelling te groot is; 4) GD-OES nog niet het niveau heeft bereikt van een routinematige techniek voor de analyse van zink-gebaseerde lagen.

D. Bijdrage van het project in een context van ondersteuning aan het proces inzake normalisatie en technische regelgeving

a) Een experimentele procedure complementair aan de ISO-norm in voorbereiding, die de implementatie van deze norm kan ondersteunen. De procedure zal verspreid worden via dit rapport en via een Vito-rapport gebaseerd op dit rapport.

b) Ervaring met de toepassing van RF GD-OES voor de bepaling van dikte en samenstelling van zink-gebaseerde lagen op staal. Kennis en infrastructuur van Vito en Certech staan ter beschikking van derden, voor de uitvoering van contractwerk.

c) Bewustmaking van de nood aan een procedure voor het meten van kraterdieptes m.b.v. een profilometer. Zelfs de beste norm voor GD-OES is waardeloos wanneer de relatieve sputtersnelheden niet correct worden bepaald. Onze resultaten werden voorgesteld op een gebruikersbijeenkomst van Jobin-Yvon, in aanwezigheid van een internationaal expert, tevens lid van het ISI/TC201.

d) Bewustmaking van het feit dat een relatieve sputtersnelheid van een kalibratiemonster aanzienlijk kan variëren en dat deze variaties niet enkel te wijten zijn aan fouten bij het meten van de kraterdieptes. Onze resultaten werden o.a. besproken op een gebruikersbijeenkomst van Jobin-Yvon. Een bijkomende inspanning zal worden gedaan om de resultaten verder te onderbouwen en te publiceren.

e) Bewustmaking van het feit dat verschillende Europese laboratoria interesse hebben om GD-OES toe te passen op zink-gebaseerde lagen, of dit reeds doen, maar dat er duidelijke problemen zijn op het vlak van kalibratie en op het vlak van integratie van de diepteprofielen.

E. Trefwoorden

GD-OES; gloei-ontlading; spectrometrie; normalisatie; deklaag; zink; staal

RESUME

A. Contexte

Une méthode de détermination de l’épaisseur et de la composition de revêtements à base de zinc déposés sur acier a été mise au point dans le cadre d’un projet de normalisation financé par le gouvernement fédéral belge. Cette méthode est basée sur la spectroscopie optique à décharge luminescente (RF GD-OES) et elle fait appel à des équipements, logiciels et échantillons de référence disponibles sur le marché.

B. Objectifs

Les objectifs du projet GAMeS étaient de 1) développer et appliquer une méthode expérimentale, basée sur la technique RF GD-OES, afin de déterminer la composition et l’épaisseur de revêtements à base de zinc déposés sur acier ; 2) identifier et décrire les facteurs critiques de l’analyse qui pourraient s’opposer à l’adoption des techniques DC et RF GD-OES en tant qu’outils de routine pour l’application envisagée, dans l’industrie métallique ; 3) créer un lien entre la Belgique et le reste du monde pour ce qui concerne ces techniques.

Le travail de recherche réalisé dans ce cadre a couvert les aspects suivants : sélection des échantillons adéquats, des éléments à analyser, des gammes de concentrations, des lignes spectrales ; optimisation des paramètres analytiques ; choix des échantillons de calibration, et détermination de leur densité et de leur vitesse d’érosion ; réalisation de courbes de calibration, de profils de composition, détermination d’épaisseur et de composition ; comparaison avec l’analyse ICP ; comparaisons inter-laboratoires portant sur la vitesse d’érosion (à échelle réduite), et sur les déterminations d’épaisseur et de composition.

C. Conclusions

Les résultats obtenus sur des échantillons industriels de type « galvanisé » et « galvannealed », en utilisant la procédure décrite dans ce rapport, sont satisfaisants et en bon accord avec les résultats obtenus généralement par analyse ICP. Les courbes de calibration pourraient toutefois encore être améliorées par l’application d’une correction de type « dc bias ».

Les comparaisons inter-laboratoires suggèrent les observations suivantes : 1) les vitesses d'érosion relatives ne sont pas nécessairement des données universelles qui peuvent être tabulées et échangées entre utilisateurs ; 2) il est urgent d'uniformiser la méthode d'obtention des vitesses d'érosion à partir des données profilométriques ; 3) la dispersion des résultats des mesures d'épaisseurs et de composition est trop importante ; 4) la spectroscopie GD-OES n'est pas considérée comme un outil de routine suffisamment précis pour l'analyse de revêtements à base de zinc.

D. Apport du projet dans un contexte d'appui aux processus de normalisation et de réglementations des techniques

a) Une procédure expérimentale complémentaire au standard ISO en préparation, qui peut contribuer à la mise sur pied de ce standard. Cette procédure sera diffusée via ce rapport et via un rapport issu du Vito, sur base de celui-ci.

b) L'expérience de l'application de la spectroscopie RF GD-OES en vue de déterminer l'épaisseur et la composition de revêtements à base de zinc déposés sur acier. L'expertise et l'instrumentation du Certech et du Vito sont disponibles en vue de la prestation de service à des tiers.

c) La prise de conscience de la nécessité d'une procédure pour la mesure de profondeur de cratères au moyen d'un profilomètre. L'utilisation des meilleurs standards perd tout intérêt si les profondeurs de cratères, et donc les vitesses d'érosion relatives, sont mesurées de façon incorrecte. Les résultats obtenus ici ont été présentés à une réunion d'utilisateurs de Jobin-Yvon, en présence d'un expert international, membre de l'ISO/TC 201.

d) La prise de conscience du fait que la vitesse d'érosion relative d'un échantillon de calibration peut varier de manière significative et que ces variations ne sont pas dues uniquement à des erreurs lors de la mesure des profondeurs de cratères. Les données collectées ont fait l'objet de discussions avec un expert international dans ce domaine et avec un utilisateur industriel belge. Les résultats ont également été présentés à une réunion d'utilisateurs de Jobin-Yvon. Ce travail sera poursuivi afin d'étoffer et de publier les constatations exposées brièvement dans le présent rapport.

e) La mise en évidence du fait que de nombreux laboratoires européens sont intéressés par l'application de la technique GD-OES aux revêtements à base de zinc déposés sur acier, ou l'utilisent déjà, mais que des problèmes existent au niveau de la calibration et de l'intégration des profils de composition. Les résultats de la comparaison inter-laboratoire seront diffusés à tous les participants et discutés avec des membres actifs de l’ISO/TC 201.

E. Mots-Clés

GD-OES; spectroscopie; décharge luminescente; normalisation; revêtement; zinc; acier

1 INTRODUCTION

This report presents the results obtained in the framework of a Belgian standardization effort - the project GAMeS (Glow-Discharge Optical Emission Spectrometry for the Analysis of Metallic Coatings on Steel) - funded by the Belgian Science Policy (contract n° NM/67/21). Project partners were Certech (Seneffe, Belgium) and Vito (Mol, Belgium). The project was coordinated by Vito. The follow-up committee consisted of Richard Payling (an international expert in the field of GD-OES) and of representatives from Ocas (Chris Xhoffer) and Cockerill-Sambre (Michel Dubois). The project ran from 01/01/2000 till 28/02/2003.

The successful development and production of protective layers on steel in general and of zinc-based coatings on steel in particular, requires accurate, reliable, fast and relatively sensitive techniques for the determination of thickness and chemical composition. For zinc-based coatings, the conventional analytical approach is to chemically dissolve the coating and to analyze the chemical solution with inductively coupled plasma optical emission spectrometry or mass spectrometry (ICP-OES, -MS). This approach has a number of disadvantages: it uses aggressive chemicals, it is relatively slow, it is difficult to apply to coatings with an increased iron-content, it is not standardized. On the other hand it has the advantage that it is a well established method in a conservative industry. One of the few potentially suitable alternative techniques is glow discharge optical emission spectrometry (GD-OES). GD-OES is a fast sputtering technique (µm/min) capable of multi-element depth profiling in a wide compositional range (0.0001 – 100 wt%). GD-OES involves the following processes (cfr. ISO/CD 16962):

a) Cathodic sputtering of a surface in a direct current or a radio frequency glow discharge device. Argon is used for sputtering.
b) Excitation of the analyte atoms in the plasma formed in the glow discharge device.
c) Spectrometric measurement of the characteristic emission spectral lines of the analyte atoms as a function of sputtering time (=depth profile).
d) Conversion of the qualitative depth profile (intensity versus sputtering time) to a compositional depth profile (mass fraction versus depth).

The latter process of conversion is not trivial at all and requires a number of preparatory steps and calibrations, as well as algorithms usually implemented by the manufacturer in the instrument’s software.

So-called radiofrequency (RF) GD-OES has the advantage over the more widespread (at least in the steel industry) direct current (DC) GD-OES, in that it can also be applied to nonconductive materials. For an introduction to the principles and applications of (RF) GD-OES we refer to the paper by Payling (1998). For a more detailed discussion about all aspects of GD-OES - both fundamental and practical - we refer to the text book edited by Payling et al. (1997).

The objectives of the project GAMeS were 1) to master an experimental method, based on RF GD-OES, to determine composition and thickness of zinc-based coatings on steel; 2) to recognize and describe critical factors in the analysis that could prevent both DC and RF GD-OES from becoming a routine tool in the steel industry for the envisaged application; 3) to link up Belgium with the rest of the world as far as GD is concerned.

Some years ago a number of larger initiatives were started on a European and international level for the standardization of GD-OES in general, and for its application to zinc-based coatings in particular, e.g. Bengtson et al. (1999). Today, this has led to a general ISO-standard (ISO 14707:2000 Surface chemical analysis – Glow discharge optical emission spectrometry (GD-OES) – Introduction to use), to a CEN standard under approval (prEN 10318 Determination of thickness and chemical composition of zinc- and aluminium-based metallic coatings – Routine method) and to an ISO-standard under approval (ISO/CD 16962 Surface chemical analysis – Determination of thickness and chemical composition of zinc and/or aluminium based coatings by glow discharge optical emission spectrometry). Unfortunately and unlike ISO/CD 16962, prEN 10318 does not address RF GD-OES.

It is not the purpose of this report to describe formally all the experimental steps required, because obviously this will be covered by the standards that will be available soon. This report is complementary to these standards in that it gives practical information and shows actual results obtained on industrial coatings.

2 METHODOLOGY

2.1 General

The different experimental steps required to obtain the average composition of a coating on a substrate by means of compositional depth profiling in RF GD-OES can be summarized as follows:

a) Identify all elements to be analysed and the concentration range for each of these analytes.
b) Select suitable spectral lines for each analyte.
c) Select and procure calibration samples.
d) Optimize analysis conditions.
e) Characterize calibration samples (density, sputtering rate).
f) Set up calibration and calibrate.
g) Obtain qualitative depth profile and convert to compositional depth profile.
h) Fix integration boundaries and integrate to obtain total coating weight for each analyte.

2.2 Selection of test samples

Two types of metallic coatings of high relevance for the Belgian steel industry were selected at the kick-off meeting of GAMeS, in the presence of all the members of the follow-up committee. It was decided to limit the scope of the project to zinc-based coatings with Zn, Al and Fe as the main constituents. It was further decided that the first type of coatings should be galvanised coatings, while the second type should be galvannealed coatings. The analysis of galvanised coatings with GD-OES was believed to be more or less straightforward, while the analysis of galvannealed coatings was stated to be a challenge. The industrial partners provided input on the range of thicknesses and compositions of galvanised and galvannealed, as well as on the compositions of the steel substrates. This information is summarised in Tables I and II. Schematic representations of galvanised and galvannealed are shown in Figure 1. A representative coating of each type was provided by Ocas. These two coatings were the initial test samples with which the method was developed. They will further be denoted as GI and GA.

In a later stage of the project other galvanised and galvannealed coatings were analysed. They differed in both composition and thickness. All coatings were of industrial relevance and were provided by Ocas. The purpose of these analyses was to check the consistency of the GD-OES results as compared to the results of ICP spectrometry. ICP-MS analyses were performed by Ocas. ICP-OES on GI and GA was performed by Certech.

Table I. Range of thicknesses and compositions of galvanised and galvannealed coatings relevant for GAMeS.

	Phase	**Galvanised**	**Galvannealed**
Thickness (µm)		5 – 20	5 – 12
Al (wt%)	**average** intermetallic layer	0.1 – 0.6 10 – 50	0.1 – 0.3 -
Fe	**average** intermetallic layer Dzeta Delta Gamma	0 – 0.5 30 – 35 - - -	7 – 12 0 – 8 6 – 12 15 – 35 (t < 2µm)
Mn		< 0.4	< 0.1
Si		< 0.07	< 0.07
Cr		< 0.07	< 0.07
Pb		< 0.05	< 0.05
Sb		< 0.05	< 0.05
P		< 0.05	< 0.05
S		< 0.05	< 0.05

Table II. Substrates and substrate compositions relevant for GAMeS.

Wt%	**Commercial**	**DDQ**	**High Strength**
C	< 0.05	< 0.005	-
Al	0.03 – 0.06	0.03 – 0.05	-
Mn	0.15 – 0.35	0.1 – 0.25	1.5
Si	< 0.01	< 0.01	0.3
Cr	< 0.03	< 0.03	0.2
P	< 0.02	< 0.02	0.07
Ti	< 0.001	0.04 – 0.07	-

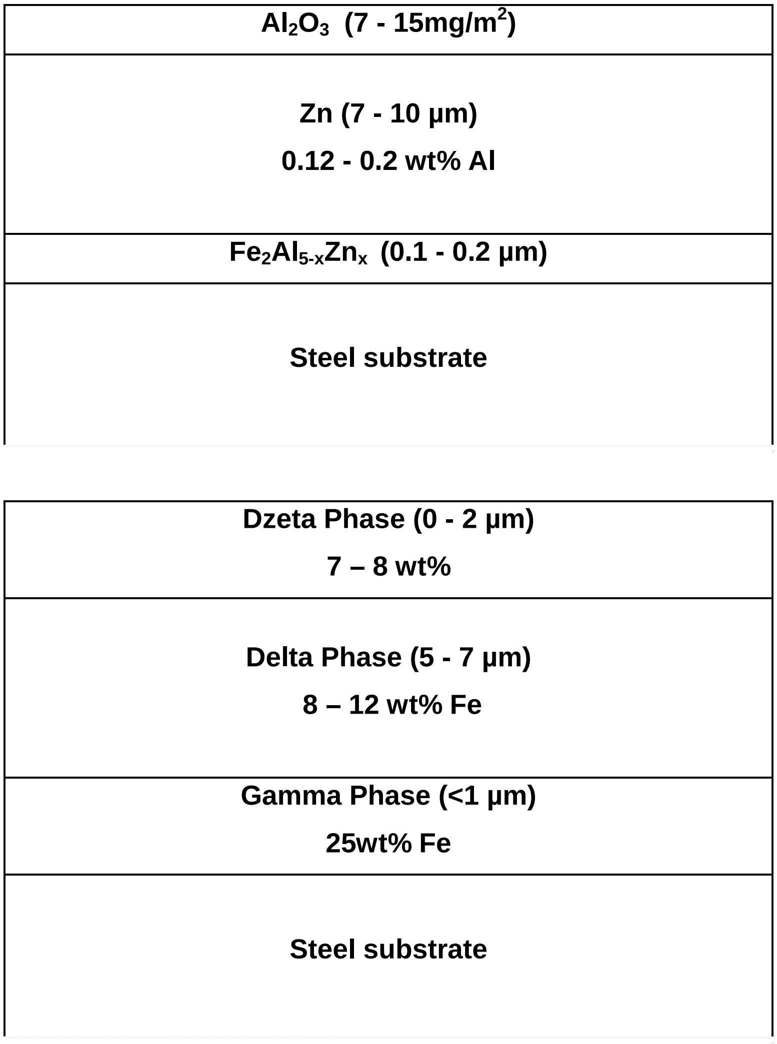


Figure 1. Schematic representations of galvanized (top) and galvannealed (bottom) coatings.

2.3 Equipment

2.3.1 GD-OES equipment

All the GD experiments were done on two instruments: a Jobin-Yvon 5000 RF (Vito) with a 500 mm focal length polychromator and a Jobin-Yvon 10000 RF (Certech) with a 1000 mm focal length polychromator (Certech). Both polychromators are nitrogen purged. Both instruments have a monochromator. Both instruments are dedicated RF instruments with a radiofrequency source of 13.56 MHz. Standard diameter of the copper anodes is 4mm. This diameter was used for all the experiments. Both instruments are equipped with a chiller for reproducible sample cooling during measurement. The cooling is done by means of a so-called cooling puck attached to the back of the sample, through which the cooling fluid (a distilled water/ethanol mixture) circulates.

During the course of the project one of the members of the follow-up committee (Ocas) also installed a GD-OES, viz. a Spectruma GDA 750. It was set up for the same applications, but in DC mode.

2.3.2 Additional equipment and its use in the project

- Scanning electron microscopes (SEM), viz. a Jeol JSM-6340F (Vito) and a FEI ESEM XL30 (Certech), with energy dispersive systems for analysis of the characteristic X-rays (EDXA) attached. Used for visualizing the morphology of the coatings (surface and cross-section) and for a first look at the element distribution in the coatings via EDXA line scans (cross-section). The cross-sections were prepared by cutting, embedding and polishing.
- A contact profilometer with diamond stylus (UBM, Vito) and a white light profilometer (Cotec, Certech). Used for measuring shapes and depths (or volumes) of craters sputtered with GD-OES. An extremely important and necessary tool when setting up methods for compositional depth profiling.
- ICP-OES (Thermo Iris Advantage). Used for analysis of GI and GA. Note: Since we had to dissolve the coatings on top and bottom of a substrate together, our ICP-results are not directly comparable with our GD-OES results, nor with the ICP-results of Ocas; they are roughly double those values. Ocas uses a dissolution method that allows them to dissolve the coating on either side of a substrate separately.

2.4 Spectral lines

The “traditional” spectral lines for most of the elements of interest are also suitable for the analysis of zinc-based coatings. Table III is an overview of relevant elements and suitable spectral lines on the polychromators of Vito and Certech. Note that elements additional to the ones in Tables I and II are listed here and that they were effectively included in the calibration. This was to assure applicability of the resulting method to a wider range of zinc-based coatings; e.g. to Zn-Ni coatings. Comments about self-absorption behaviour of the spectral lines are given. Self-absorption causes non-linear calibration curves at high analyte concentration levels. Strongly self-absorbed lines should therefore be avoided for the major elements. Detailed information about optical emission lines, their relative intensities and their self-absorption behaviour can be found in the book by Palyling and Larkins (2000).

Table III: Elements and suitable spectral lines on the polychromators of Vito and Certech.

Element	Wavelength of spectral line (nm)		Comment
	Vito	Certech	
Zn	481.05	334.40	
Al	396.15	396.15	Self-absorption
Fe	371.94	371.94	Weak self-absorption
C	156.14	156.14	
Ti	365.35	337.28	
Si	288.16	288.16	
Sb	259.81	231.15	
S	180.73	180.73	
Pb	220.35	220.35	
P	178.29	178.29	
Ni	341.78	341.78	Weak self-absorption
Mn	403.45	403.45	
Mg	383.83	280.27	
Cu	327.40	327.40	Strong self-absorption
Cr	425.43	425.43	
Co	-	345.35	
Ca	-	393.37	

2.5 Optimum analysis parameters

Most commercial RF GD-OES instruments, such as the ones used in this project, are operated with constant applied power (W) and constant source pressure (Pa). These two source parameters must be chosen in such a way that a good depth resolution is obtained, preferably in combination with adequate sputtering. Good depth resolution implies sputter craters with flat bottoms. Adequate sputtering means as fast as possible without over-heating the coating. An additional means to avoid over-heating is to cool the sample during measurement.

After discussions with Richard Payling, we used the following procedure to optimize source parameters for depth profiling of zinc-based coatings:

a) Select a combination of power and pressure that gives a penetration rate in the range 2-3 µm/min in low alloy steel (e.g. in SRM 1767). This avoids conditions were too much energy is being put into the zinc-based coatings.

b) Apply these conditions of power and pressure to a brass sample or to an actual test sample and sputter to a depth of 10-40 µm (but still inside the coating in the case of a test sample). Verify the crater shape with a profilometer. If the crater is convex (=rounded bottom) the source pressure is too high. If the crater is concave (=deep sides) the source pressure is too low. Keep the power constant, adjust the pressure, sputter a fresh crater and verify the crater shape. Repeat until a flat crater bottom is obtained. Use the final value of the pressure for the actual experiments.

For the JY 5000RF and the JY 10000RF suitable analysis parameters were found to be:

a) power 30-40 W;
b) pressure 600-750 Pa;
c) temperature of the cooling puck: 10-15°C.

2.6 Calibration

Calibration consists in determining for the selected spectral line of each analyte, the so-called analytical response curve. The curve is obtained by regression analysis of the calibration data. The curve relates emission intensity of the spectral line of an analyte in a calibration sample to the concentration of the analyte in that sample, taking into account differences in sputtering rates. Calibration requires the knowledge of the chemical composition and the sputtering rate of all calibration samples.

2.6.1 Selection of calibration samples

Calibration samples have to cover the whole concentration range, i.e. from zero to the highest concentrations to be determined, for all analytes. In order to have sufficient points on the calibration curves at least five calibration samples should be measured for each analyte. The ideal calibration samples are spectrometric calibration samples issued as certified reference materials (CRMs). In practice one sometimes has to do with less.

There was a consensus (after discussions with Richard Payling in our follow-up committee) that a minimum set of calibration samples for the analysis of zinc-based coatings should consist of the following:

a) One high purity copper sample with concentrations of the analytes below 0.001 mass%. This sample can be used as a zero point for all analytes except copper, even when its exact composition is not known.
b) At least two brass samples with zinc contents of 25 to 50 mass%; aluminium contents of 1 to 4 mass%; lead contents of 1 to 4 mass%.
c) At least two zinc-aluminium alloys with a zinc content of 40 to 95 mass%.
d) At least one aluminium-silicon alloy with a silicon content of 5 to10 mass%.
e) At least one nickel based alloy with a nickel content of more than 70 mass%.

f) At least two stainless steel samples with nickel contents of 10 to 40 mass%.

g) At least one pure iron or low alloy steel sample to be used as sputtering rate reference.

The use of zinc-aluminium alloys with more than 95 mass% zinc is generally discouraged, because of potential non-reproducibility of sputter rates. On the other hand one should bear in mind that the actual test samples can contain well over 95 mass% of zinc. The zinc-rich CMI samples (Table IV) were included in the calibrations of Vito.

The RMs used for calibration in this project are listed in Tables IV, V and VI. For each RM the concentrations are given of the most important elements for this calibration.

Table IV. Calibration samples used in this project. V=Vito, C=Certech.

	Certified by	**Used by**	**Zn**	**Al**	**Fe**	**Ni**	**Pb**	**Si**
Pure copper:								
3563	-	V/C	< 5 ppm	< 5 ppm	7 ppm	< 5ppm	< 5 ppm	
Brass:								
31X B22	MBH	V/C	(15.2)	0.22	0.16	0.14	0.15	
L 3	CTIF	V/C	32.70	0.91	0.36	0.90	1.02	0.034
L 4-1	CTIF	V/C	34.60	0.102	0.466	0.227	2.017	0.12
L 7	CTIF	V/C	42.45	0.308	0.031	0.020	0.71	0.13
LH 11	CTIF	V/C	26.20	0.46	0.36	2.91	1.26	0.88
LH 13	CTIF	V/C	31.8	2.00	(2.00)	3.22	0.67	0.21
Zn-based:								
43X Z1	MBH	V/C	(94.9)	4.51	0.008	0.001	0.003	-
43X Z11	MBH	V/C	(87.0)	12.20	0.086	-	0.034	-
43X Z13	MBH	V/C	(89.3)	9.58	0.06	-	0.012	(0.004)
43X Z14	MBH	V	(90.7)	8.0	0.02	-	0.01	-
43X Z21	MBH	V/C	(72.2)	25.7	0.14	-	0.010	-
43X Z23	MBH	V/C	(64.8)	32.0	0.05	-	0.004	-
CZ2009	CMI	V	94.1	5.07	0.107	0.154	0.058	0.003
CZ2010	CMI	V	98.5	0.172	0.286	0.263	0.255	-
CZ2011	CMI	V	98.7	0.035	0.336	0.302	0.299	-
CZ2012	CMI	V	78.7	20.1	0.027	0.074	0.081	0.37
CZ2013	CMI	V	42.9	52.8	0.120	0.539	0.49	1.07
CZ2014	CMI	V	97.5	0.967	0.023	0.409	0.046	0.002
Al-based:								
AA356.0	Alcan	V	0.037	(92.7)	0.23	0.038	0.038	5.80
AA356.2	Alcan	V	0.075	(91.7)	0.16	0.033	0.017	7.20
AA339.1	Alcan	V	0.044	(82.9)	0.40	0.68	0.031	12.04
55XG28J5	MBH	C		69.15				
55XG02D6	MBH	C		83.86				
55XG900J3	MBH	C		96.15				

Table V. Calibration samples used in this project. V=Vito, C=Certech.

	Certified by	**Used by**	**Al**	**Fe**	**Cr**	**Ni**	**C**	**Si**
Ni-based:								
SS 351	BAS	V/C	0.55	18.26	18.12	53.1	(0.025)	0.14
28X6005	MBH	V/C	0.05	7.12	16.80	-	-	0.65
28X6002	MBH	V/C	0.18	8.24	16.23	-	-	0.25
219M 600C	Brammer	V/C	0.20	9.30	15.62	73.59	0.072	0.39
219M 825B	Brammer	V/C	0.10	35.1	20.06	38.7	0.024	0.24
Stainless Steel:								
SS 463/1	BAS	V	-	(68.9)	18.46	10.20	0.019	0.27
SS 464/1	BAS	V	-	(53.0)	25.39	20.05	0.086	0.57
SS 465/1	BAS	V	0.026	(70.8)	17.31	9.24	0.066	0.405
SS 466/1	BAS	V	0.062	(70.2)	17.65	8.61	0.062	0.505
SS 474	BAS	V	-	(60.0)	19.06	14.74	0.022	0.17
SS 475	BAS	V	-	(75.0)	14.14	5.66	0.050	0.21
S19	RIFM	C		(76.1)		12.8		
S20	RIFM	C		(71.5)		18.2		
S21	RIFM	C		(67.1)		22.3		
S22	RIFM	C		(68.8)		28.2		
S23	RIFM	C		(65.4)		33.4		
S24	RIFM	C		(75.6)		9.19		
S25	RIFM	C		(64.7)		13.8		
S26	RIFM	C		(73.1)		3.3		
S27/1	RIFM	C		(63.9)		6.1		

2.6.2 Surface preparation of calibration samples

For consistency and reproducibility of the results it is important that an RM is always ground and polished to the same surface finish and that the surface finish is the same for all RMs. In practice a wet polish with P600 SiC paper is very often sufficient and was used routinely by Vito throughout this project. After polishing, the samples were wiped with ethanol using a lint free cloth.

Certech additionally applied a procedure with seven polishing steps of which the last one is a high quality surface finish with 1 µm diamond slurry. The final surface quality is much higher, but the procedure is lengthy and is therefore difficult to apply on a routine basis. There was no apparent improvement of the calibration data.

Table VI. Calibration samples used in this project. V=Vito, C=Certech.

	Certified by	**Used by**	**Al**	**Fe**	**C**
Low Alloy Steel:					
SRM 1761	NIST	V	0.055	(95.1)	1.03
SRM 1763	NIST	V	0.043	(94.5)	0.203
SRM 1765	NIST	V	-	(99.6)	0.006
SRM 1766	NIST	V	-	(99.8)	0.015
SRM 1767	NIST	V	0.004	(99.8)	0.052
180A	CMI	C		(99.98)	
181A	CMI	C		(95.48)	
182A	CMI	C		(94.6)	
183A	CMI	C		(94.49)	
184A	CMI	C		(93.58)	
185A	CMI	C		(93.63)	
186A	CMI	C		(93.06)	
187A	CMI	C		(93.01)	
188A	CMI	C		(90.53)	
189A	CMI	C		(90.01)	

2.6.3 Density of calibration samples

It is recommended to measure the density of all calibration samples, except perhaps in those rare cases where the density is given on the analysis certificate. A suitable and reliable method for homogeneous bulk samples is “sample mass divided by sample volume” where the sample volume is measured by immersion of the sample in water following Archimedes’ law. An alternative method, but in general less accurate and only applicable to regularly shaped samples, is to calculate the volume from the dimensions of the sample.

If this procedure cannot be followed, a density ρ can still be calculated:

$$\rho = 100 / \sum_i m_i / \rho_i$$

where m_i is the mass percent of element i in the sample; ρ_i is the theoretical density of element i.

All three procedures were used in this project. The resulting values for the densities are referred to as “Archimedes”, “volume calculated” and “calculated”, respectively. All values are listed in Tables VII-IX.

2.6.4 Relative sputtering rates of calibration samples

The *sputtering rate* (SR) of a sample is the mass loss rate during sputtering in the glow discharge. It is generally expressed in g/m^{2}s. The *relative sputtering rate* (RSR) of a sample is the sputtering rate of the sample divided by the sputtering rate of a reference material (the “sputtering rate reference”) sputtered under the same conditions.

We strongly recommended to actually measure the sputtering rates of all calibration samples, rather than to rely on published RSR data, especially when these are poorly documented.

Different approaches are possible for determining the relative sputtering rates. This is one of the approaches used in this project:

a) Analysis parameters were set to the optimum conditions (cfr. §2.5).
b) Three craters were sputtered in each calibration sample. Sputtering times were chosen in the range 3-10 min depending on the estimated erosion rate, resulting in craters of 15-60 µm depth. In general the same sputtering time was used for samples of the same type (cfr. Tables IV-VI).
c) With a diamond stylus profilometer three profile traces in different directions across the centre of each crater were performed. For each scan a value for the depth was derived. Note that this is a weak point in the procedure: the position of the bottom of the crater has to be fixed; especially for non-flat crater bottoms (convex, concave, rough) this can be very arbitrary and operator dependent.
d) The average penetration rate (µm/s) of each sample was calculated as the average depth divided by the sputtering time.
e) The average sputtering rate per unit area (g/m^{2}s) of each sample was calculated as the average penetration rate multiplied by the density.
f) Low alloy steel SRM 1767 was chosen as the sputtering rate reference sample.
g) The average relative sputtering rate of each sample was calculated as the average sputtering rate per unit area divided by the average relative sputtering rate per unit area of the reference sample.

Results are shown in §3.3.

2.6.5 Emission intensity of calibration samples

The following procedure was used:

a) The surfaces of the calibration samples were reprepared (§2.6.2).
b) Analysis parameters were set to the optimum conditions (§2.5).

c) A preburn time or preacquisition time of typically 60-90s was used to assure that the acquired intensities were representative for the bulk of the samples.
d) A signal integration time of 10s; 4-8 repeats in one crater; 1-2 craters were used.
e) The emission intensities (in volts) of all analytes were measured for each calibration sample. Outliers were rejected manually. The relative standard deviations of the average intensities were kept typically below 1% for all analytes.
f) Calibration graphs for all analytes were inspected and calibration curves were corrected where necessary. Corrections were mainly necessary for two reasons:
    1) To force the calibration curves of an analyte through the zero point; i.e. through the point measured for this analyte in pure copper (§2.6.1).
    2) To compensate for a large separation in a calibration graph between samples with different matrices. Such a separation is due to different emission yields of the different matrices. A simple solution is to keep only those samples in the graph which most resemble the test samples. A more sophisticated solution is to measure the dc bias voltages of the calibration samples and to apply a correction factor. The latter was not possible on our instruments.

Calibration graphs for zinc, aluminium, iron and nickel are shown in §3.3.

2.7 Compositional depth profiles

Optimum analysis conditions (§2.5) were used to obtain qualitative depth profiles (sputtering time versus emission intensity). Sputtering times were in the range 180-360s. The profiles were then converted into compositional depth profiles (depth versus mass percent) literally at the touch of a button, using the underlying algorithms and calibration curves. Coating thickness and total coating weight (g/m^2) for each element were derived as follows:

a) The coatings thickness was the depth were the concentration of zinc was reduced to 50% of the average value in the coating.
b) The integration depth for all elements other than iron was taken as the sum of the coating thickness and the width of the interface region, where the width of the interface region was defined as the difference between the two points in depth were the concentrations of zinc are 84% and 16% respectively of the average value in the coating.
c) After discussions with Ocas, the integration depth for iron in galvanized coatings was chosen from zero to the point where zinc is reduced to 90% of the average value in the

coating. The integration depth for iron in galvannealed coatings was chosen from zero to the point where zinc is reduced to 80% of its initial value.

It is clear that especially the integration depth for iron is rather arbitrary. ISO 16962 is expected to put forward procedures for the calculation of the total coating weight of all elements including iron.

Examples of compositional depth profiles are shown in §3.5. Results for thickness and total coating weight are given in §3.6.

2.8 Interlaboratory comparison

For practical reasons, it was decided to limit the interlaboratory comparison to European institutes and industries. Most of the potential participants were contacted at or shortly after the final general meeting of the EC Thematic Network on Glow Discharge Spectroscopy for Spectrochemical Analysis – GDSNet. Finally, 22 laboratories – including Certech and Vito – confirmed their participation. Of these 22 labs, 15 returned data. Unfortunately, not always complete. An overview of the participants is given in §3.7.

All participants received a disk-shaped sample (diam. 30mm) of hot dipped galvanized steel, which they were asked to analyse from one side with GD-OES. The other side was marked with a felt-tip pen. The samples were provided by Ocas. The samples had to be returned to Vito after analysis, together with a report sheet. The idea behind small samples and having to return them was that none of the participants would be tempted to do ICP-spectrometry (which would destroy the whole sample) as well as GD-OES.

The participants were asked to report thickness and total coating weight for Zn, Al and Fe, as well as information on analysis parameters, calibration samples and relative sputtering rates. The participants were not given instructions about how to derive thickness and total coating weight from the compositional depth profiles. The aim was to be able to compare those results that the different labs would routinely be reporting to there customers. The results are presented in §3.7.

3 RESULTS

3.1 Morphology and element distribution

Results of SEM observations on GI and GA are shown in figures 2 - 5. Both for GI and GA the circular patterning (diameter approximately 100 µm) applied to the substrates to enhance coating adhesion is clearly visible in the surface images. The GA surface is covered with crystals of typically 1 µm in width and 5-10 µm in length. Observations on cross-sections, shown in figure 4 - 5, allow to derive an approximate local value for the thickness of the coatings. The average thickness of GI is around 9 µm, but the thickness varies between 7 and 12 µm on a length scale of only 100 µm. The average thickness of GA is approximately 7.5 µm, with local variations between 5.5 and 9 µm on the same small length scale. The length scale of the variations suggests that they are related to the patterning of the substrate. The quantitative EDXA line scans over cross-sections of GI and GA, shown in figure 6, reveal the local distribution of zinc, iron and aluminium in the coatings. EDXA is not an alternative for ICP or GD for this application, because of its time-consuming sample preparation, its local character and its limited sensitivity.

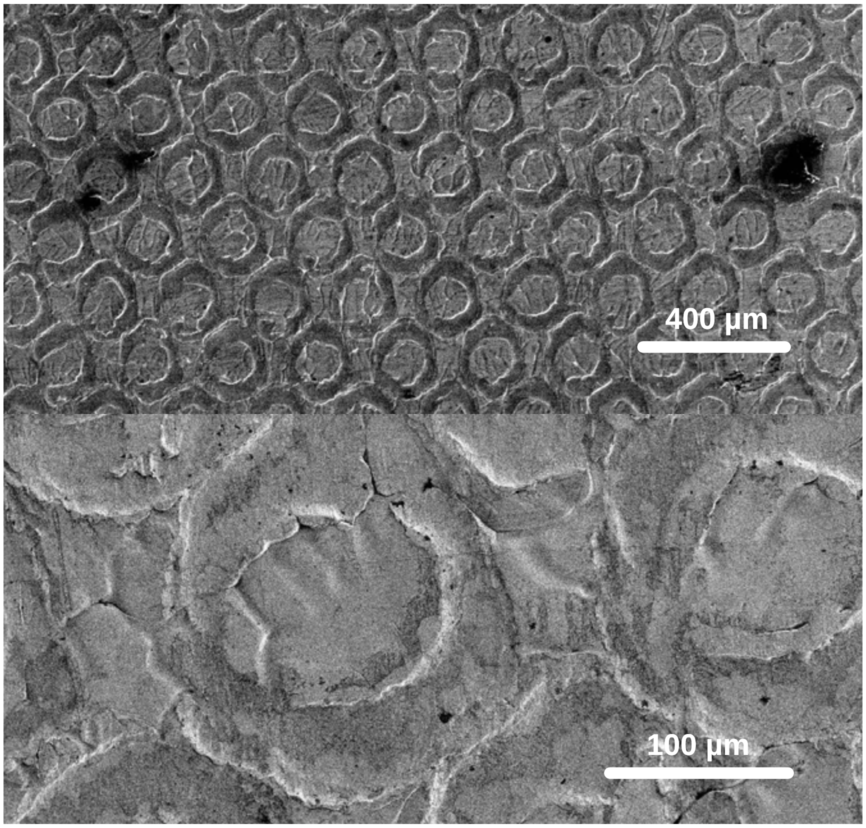


Figure 2. Morphology of the surface of coating GI as observed in SEM. Overview and detail.

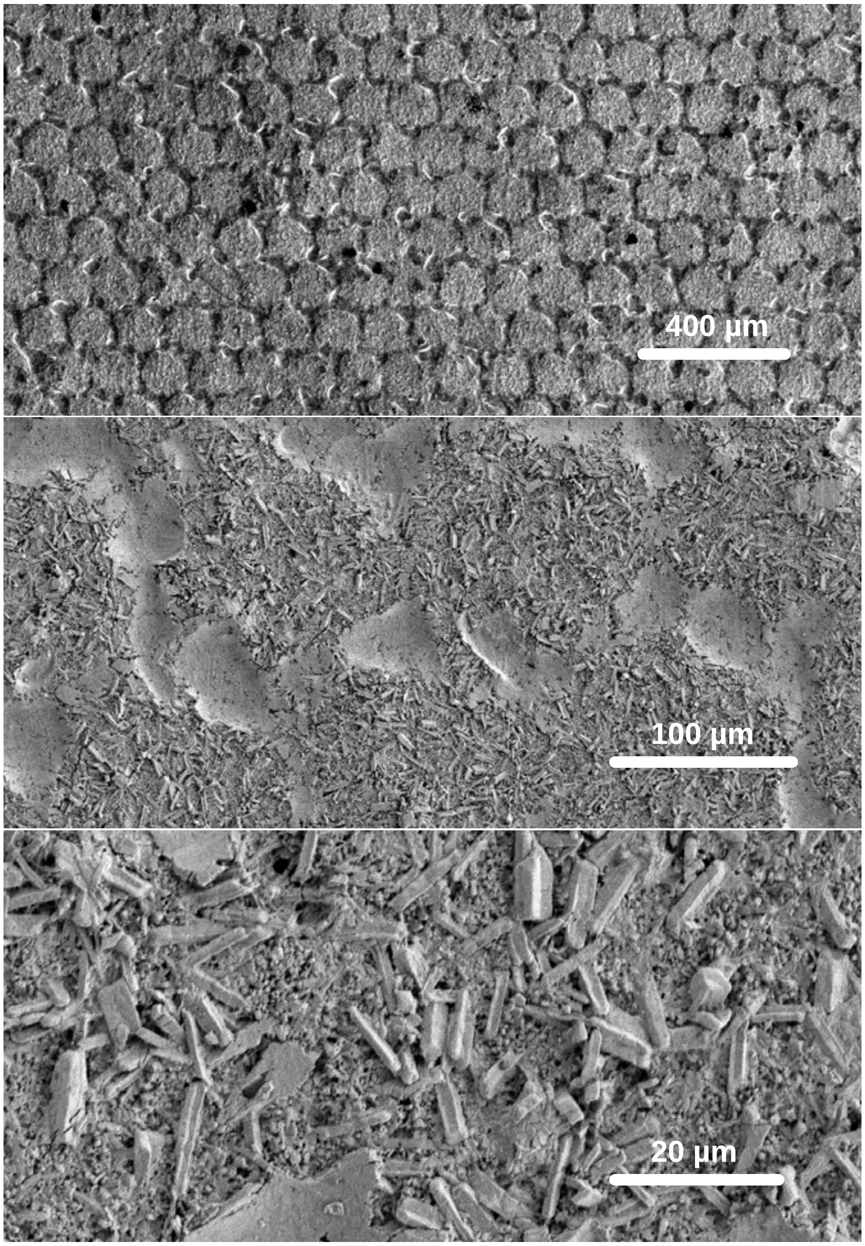


Figure 3. Morphology of the surface of coating GA as observed in SEM. Overview and details.

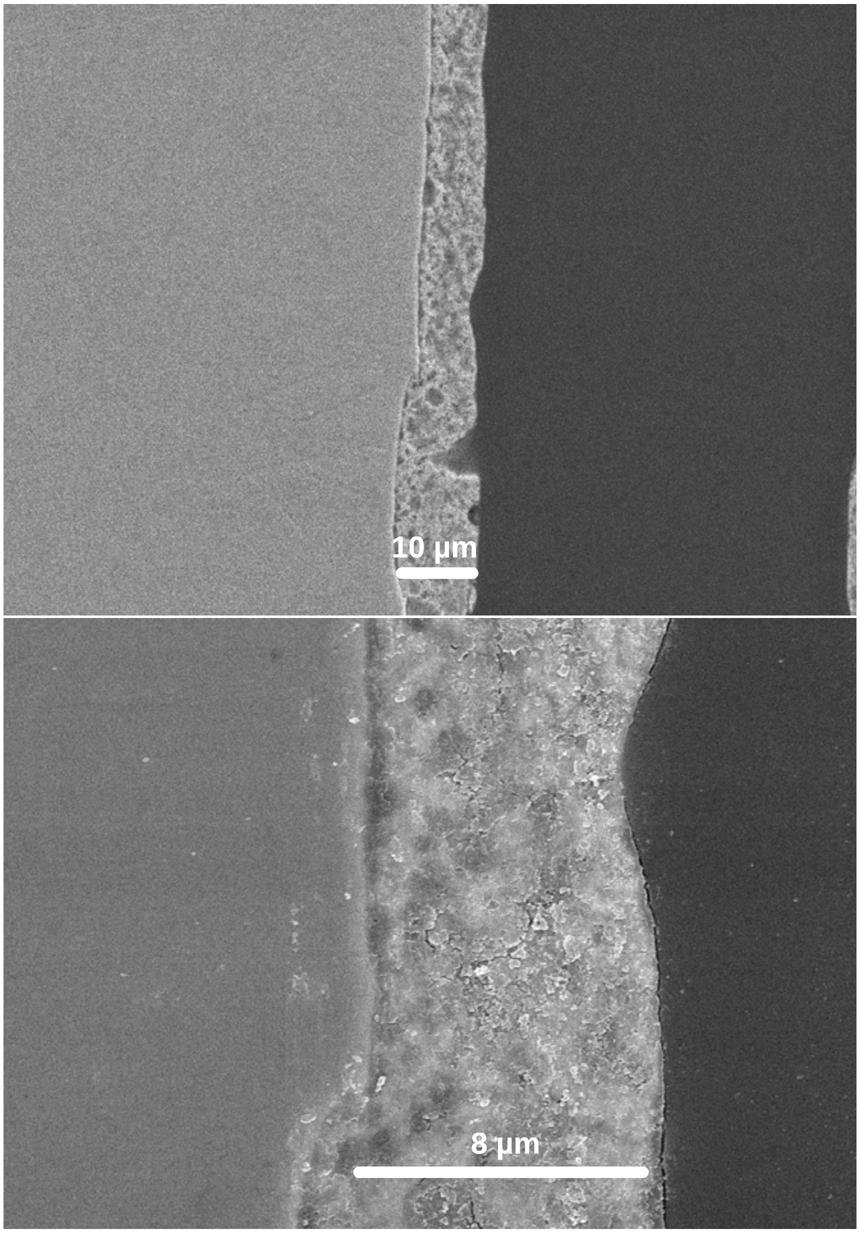


Figure 4. Cross-section of the coating GI on its substrate, as observed in SEM. Overview and detail.

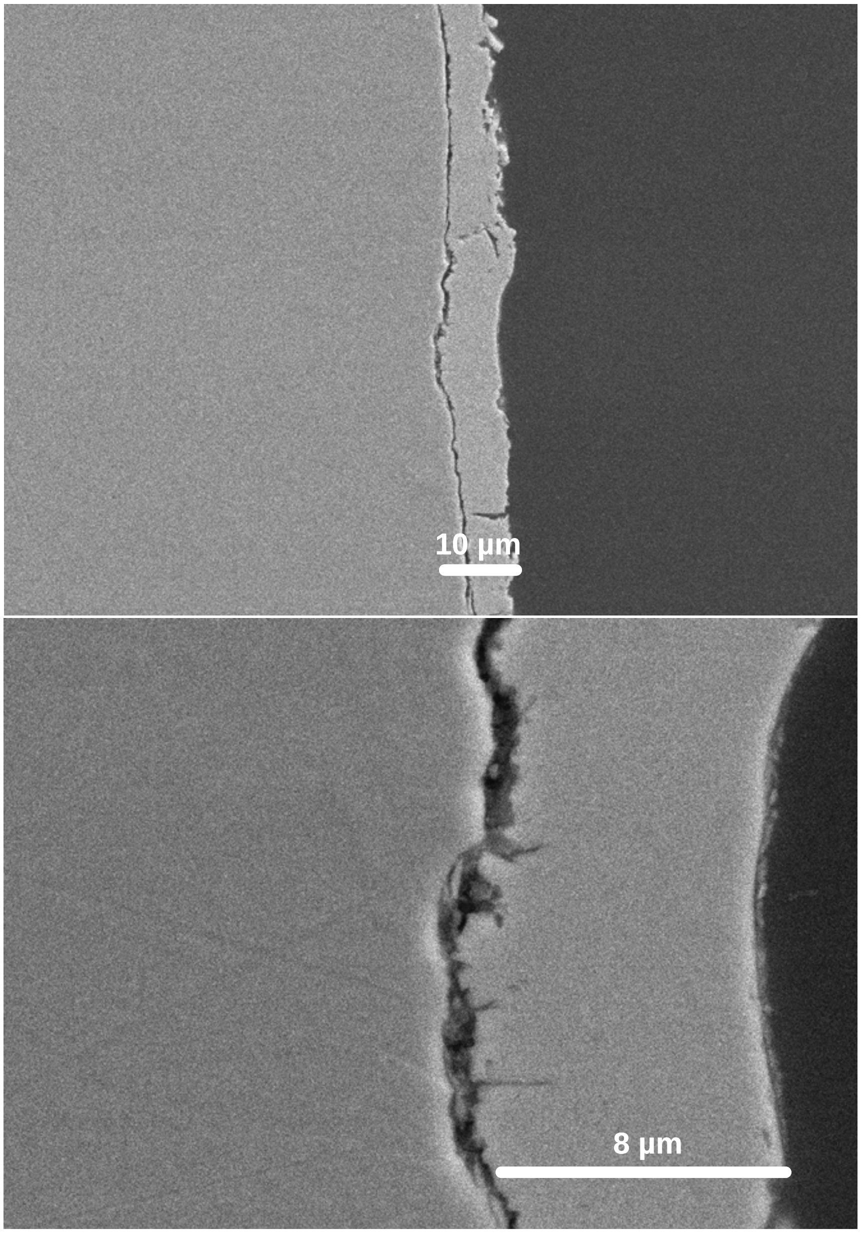
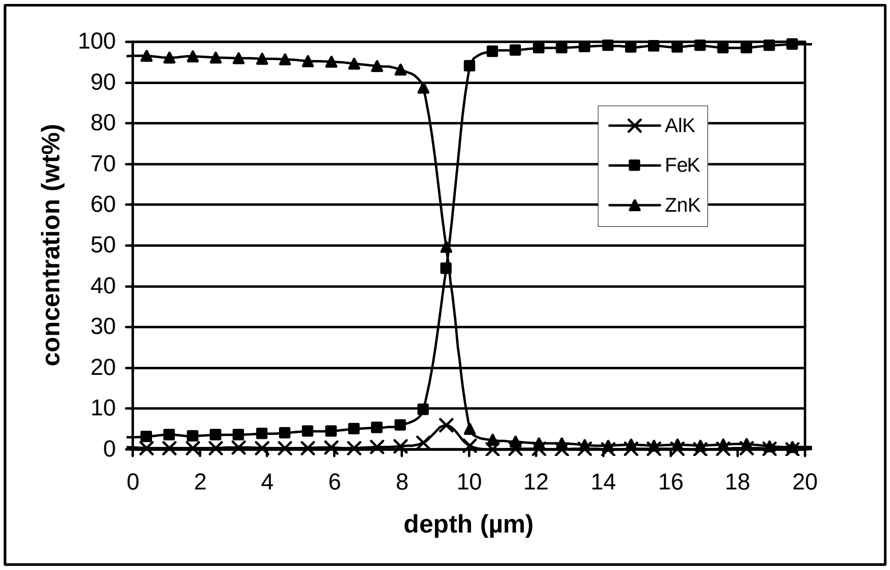


Figure 5. Cross-section of the coating GA on its substrate, as observed in SEM. Overview and detail.



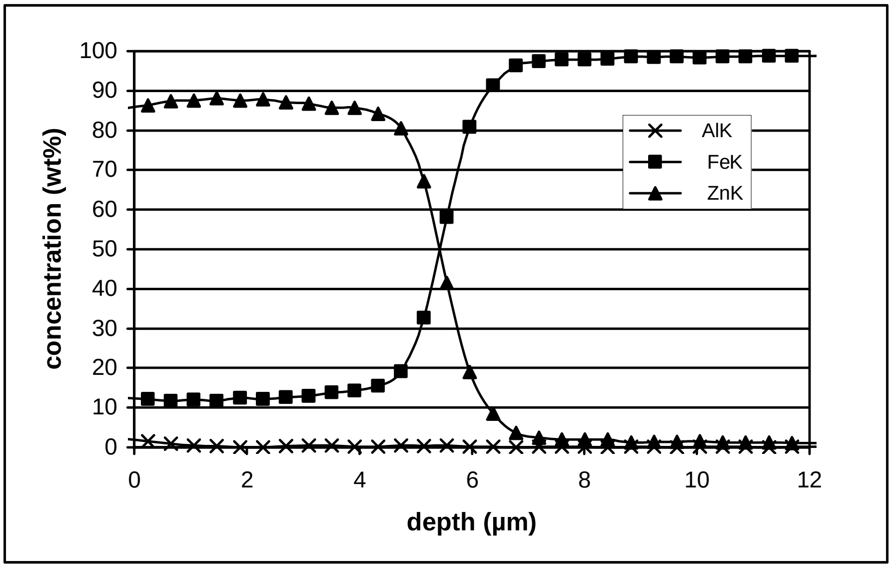


Figure 6. EDXA line scans over the cross sections of GI (top) and GA (bottom).

3.2 Densities of calibration samples

Values for the densities of all calibration samples are listed in Tables VII - IX. Three values are given, viz. “Archimedes”, “volume calculated” and “calculated” (cfr. 2.6.3). There is a good to excellent agreement between the different values, with differences well below 5%. The values “Archimedes” and “volume calculated” were used in the calculations of the relative sputtering rates.

Table VII. Densities and relative sputtering rates of calibration samples.

	Density (g/cm^3)			**Relative sputtering rate**	
	Archimedes	volume calculated	calculated	Vito 40W, 750Pa	Certech 30W, 600Pa
Pure copper:					
3563	8.94	8.93	8.93	3.11	3.61
Brass:					
31X B22	8.54	8.49	8.49	3.19	3.84
L 3	8.32	-	8.07	3.53	3.72
L 4-1	8.40	-	8.18	3.56	4.13
L 7	8.27	-	7.99	4.03	4.03
LH 11	8.36	-	8.10	3.07	3.39
LH 13	8.05	-	7.81	3.06	3.08
Zn-based:					
43X Z1	6.66	6.65	6.65	3.47	3.61
43X Z11	5.87	5.85	5.94	2.62	2.62
43X Z13	6.21	6.2	6.17	3.07	2.78
43X Z14	6.33	-	6.32	3.52	-
43X Z21	5.05	5.0	5.02	1.82	1.75
43X Z23	4.71	4.72	4.69	1.55	1.50
CZ2009	6.59 (CMI)		6.59	3.59	-
CZ2010	7.13 (CMI)		7.12	5.11	-
CZ2011	7.19 (CMI)		7.14	5.23	-
CZ2012	5.35 (CMI)		5.33	2.00	-
CZ2013	3.78 (CMI)		3.75	0.85	-
CZ2014	6.98 (CMI)		7.02	4.60	-
Al-based:					
AA356.0	2.70	-	2.68	0.379	-
AA356.2	2.69	-	2.67	0.363	-
AA339.1	2.73	-	2.70	0.452	-
55XG28J5	-	2.6	2.72	-	0.319
55XG02D6	-	2.70	2.83	-	0.32
55XG900J3	-	2.72	2.82	-	0.36

3.3 Relative sputtering rates

Optimum conditions for power and pressure were determined by sputtering in low alloy steel and in brass (cfr. §2.5). At 40W and 750 Pa (JY 5000RF) the penetration rate in low alloy steel SRM 1767 was typically 3.2 µm/min. Under the same analysis conditions craters with a flat bottom were obtained in brass. An example of a crater profile in brass L7 is shown in figure 7. The profile was measured with a mechanical profilometer. Although this particular crater is close to 60 µm in depth, it is recommended to limit the sputtering depth in the calibration samples to about 30 µm to avoid variations in the sputtering behaviour due to changes in the discharge conditions that might occur at increased anode-sample distances.

Relative sputtering rates for all calibration samples were derived as described in §2.6.4. They are listed in Tables VII - IX. Sputtering rates of calibration samples common to Vito and Certech were measured independently by both labs. For a number of sample types the differences are large and non-systematic. This can be due to one or a combination of factors:

a) Variations in the glow discharge due to instrumental instabilities;

b) Differences in microstructure (grain size) between chemically identical (=same composition) reference materials from different batches; this is the case for some of the brass samples.

c) Errors in the measurement of the crater depth; e.g. due to roughness of the crater bottom, due to reflective properties of the crater bottom (in the case of an optical profilometer).

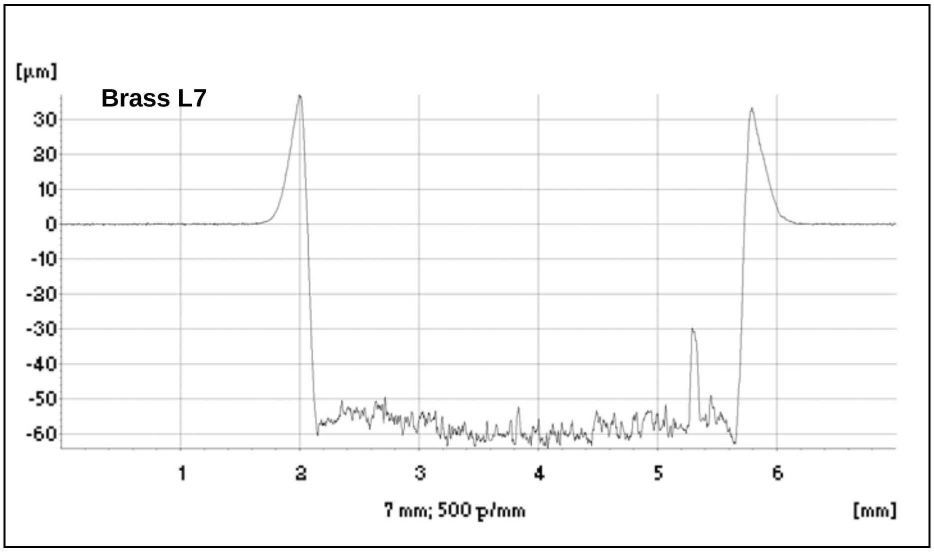


Figure 7. Example of a crater profile in the calibration sample brass L7. Crater depth is close to 60 µm. Sputtering time was 10 min.

Table VIII. Densities and relative sputtering rates of calibration samples.

	Density (g/cm^3)			**Relative sputtering rate**	
	Archimedes	volume calculated	calculated	Vito 40W, 750Pa	Certech 30W, 600Pa
Ni-based:					
SS 351	8.23	8.2	8.14	1.11	1.28
28X6005	8.38	8.36	8.30	1.25	1.53
28X6002	8.38	8.38	8.37	1.48	1.37
219M 600C	8.38	8.35	8.32	1.35	1.55
219M 825B	8.09	8.04	8.03	1.15	1.35
Stainless Steel:					
SS 463/1	7.92	-	7.76	1.08	-
SS 464/1	7.87	-	7.74	1.12	-
SS 465/1	7.90	-	7.71	1.09	-
SS 466/1	7.94	-	7.75	1.11	-
SS 474	7.99	-	7.87	1.15	-
SS 475	7.84	-	7.81	1.07	-
S19	-	7.83	7.80	-	1.10
S20	-	8.04	8.0	-	1.2
S21	-	8.04	8.04	-	1.2
S22	-	8.08	8.12	-	1.23
S23	-	8.09	8.2	-	1.22
S24	-	7.76	7.80	-	1.16
S25	-	7.85	7.81	-	1.21
S26	-	7.65	7.77	-	1.22
S27/1	-	7.64	7.63	-	1.11

An interlaboratory comparison between Vito and Ocas confirmed that the measurement of crater depth is a potential source of errors. In this comparison relative sputtering rates were determined of four CRMs. Craters sputtered by Ocas with DC GD-OES were measured (=profilo1) by Ocas and Vito. Craters sputtered by Vito with RF GD-OES were measured (=profilo2) by Vito and Ocas. The results are shown in Table X. The work was performed in the framework of a RSR interlaboratory comparison organised by Richard Payling, the results of which were not yet known when this report was written. Deviations due to profilometry are typically below 4% for BAM306 and JK37, but close to 10% for IARM-87A. This larger deviation is due to the roughness of the crater bottom, which makes its exact position very arbitrary. Deviations between the values obtained from DC and RF craters for BAM306 (12%) and JK 37 (30%) are large and require further investigation; e.g. is it possible that differences in sputtering behaviour between low alloy steel and stainless steel are much more pronounced in DC than in RF?

It is clear that one has to be extremely cautious when using RSR data from literature or from tables of manufacturers. RSR are not as universal has the GD community would wish. This is to a large extent due to the difficulty of accurately and reproducibly measuring crater depth, for which procedures should urgently be agreed, in particular for non-ideally shaped craters. A second and more fundamental reason might well be a difference in discharge conditions between different sources, in particular between DC and RF type sources.

Table IX. Densities and relative sputtering rates of calibration samples.

	Density (g/cm^3)			**Relative sputtering rate**	
	Archimedes	volume calculated	calculated	Vito 40W, 750Pa	Certech 30W, 600Pa
Low Alloy Steel:					
SRM 1761	7.81	-	7.70	0.931	-
SRM 1763	7.79	-	7.68	0.990	-
SRM 1765	7.87	-	7.87	1.03	-
SRM 1766	7.87	-	7.86	0.964	-
SRM 1767	7.87	-	7.85	1.00	1.00
180A	-	7.85	7.85	-	1.11
181A	-	7.82	7.83	-	1.10
182A	-	7.78	7.79	-	0.98
183A	-	7.76	7.83	-	1.10
184A	-	7.80	7.75	-	0.962
185A	-	7.82	7.83	-	1.08
186A	-	7.45	7.76	-	1.07
187A	-	7.8	7.86	-	1.09
188A	-	7.75	7.78	-	1.12
189A	-	7.89	8.02	-	1.21

Table X. Relative sputtering rates of four important CRMs, measured by Ocas (Profilo1) and Vito(Profilo2) on craters sputtered by Ocas (DC) and Vito (RF).

	DC Profilo1	DC Profilo2	RF Profilo1	RF Profilo2
SRM 1762 low alloy	1	1	1	1
BAM 306 Al, 8%Si, 3%Cu	0.422	0.438	0.376	0.390
IARM-87A brass	3.26	3.55	3.38	3.02
JK 37 SS: Fe,Cr,Ni,Mo	1.34	1.28	1.056	1.01

3.4 Calibration graphs : intensity versus (concentration x relative sputtering rate)

3.4.1 Calibration graphs for zinc

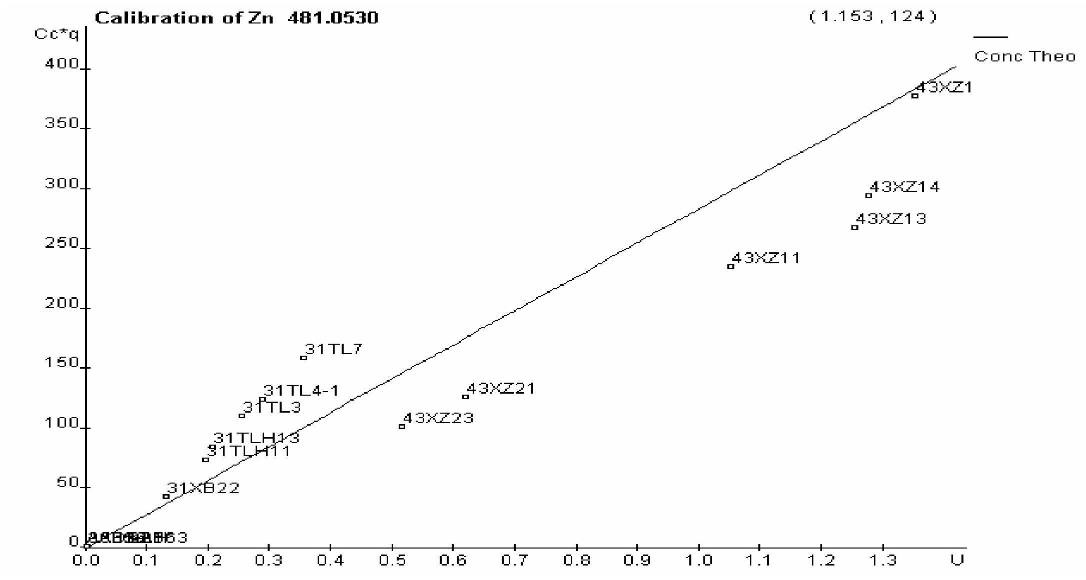


Figure 8. Calibration graph for zinc, including the brass samples. The separation between brass and zinc-aluminium matrices can clearly be distinguished (§2.6.4).

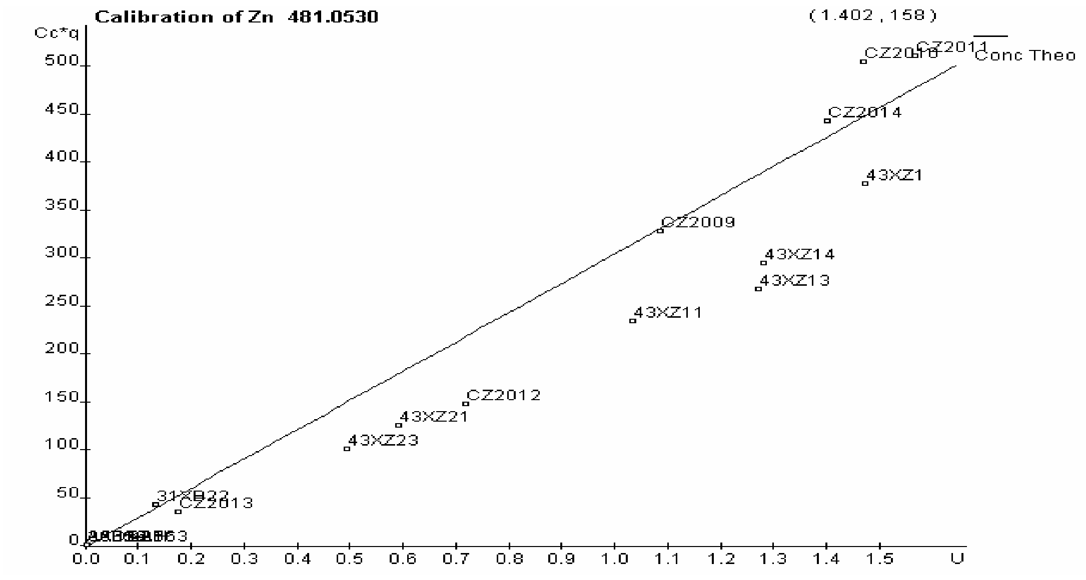


Figure 9. Calibration graph for zinc, excluding most of the brass samples, but including the zinc-rich CMI samples. Note the apparent separation between CMI and MBH zinc-alloys. The weight of the MBH samples was deliberately decreased to include some of the more zinc-rich CMI samples.

3.4.2 Calibration graph for aluminium

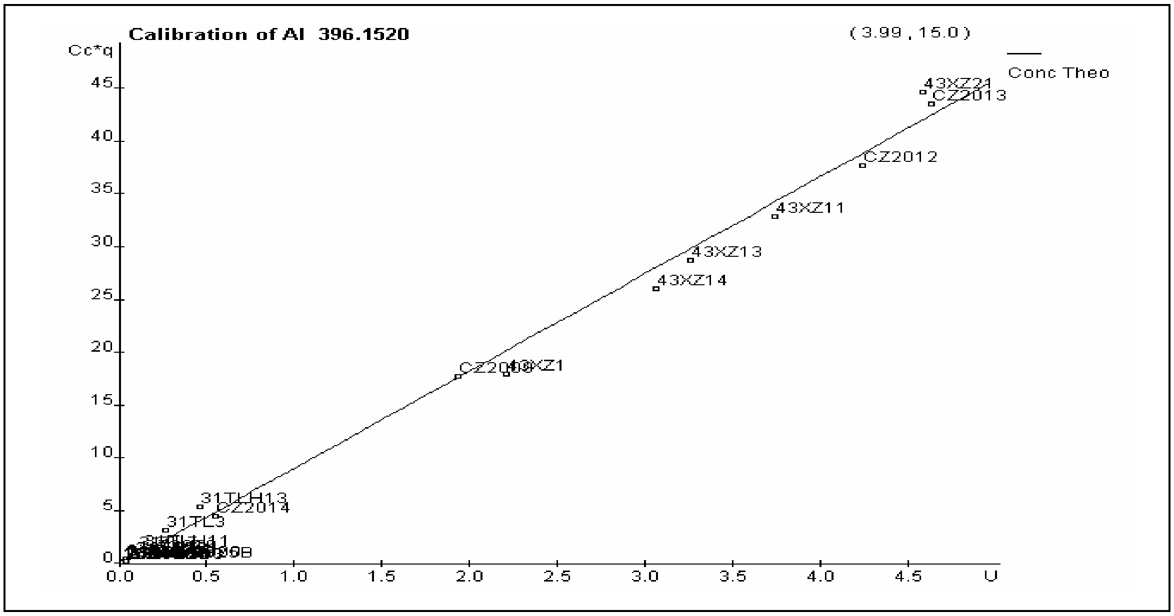


Figure 10. Calibration graph for the whole concentration range of aluminium in the calibration samples. Aluminium-silicon alloys were excluded.

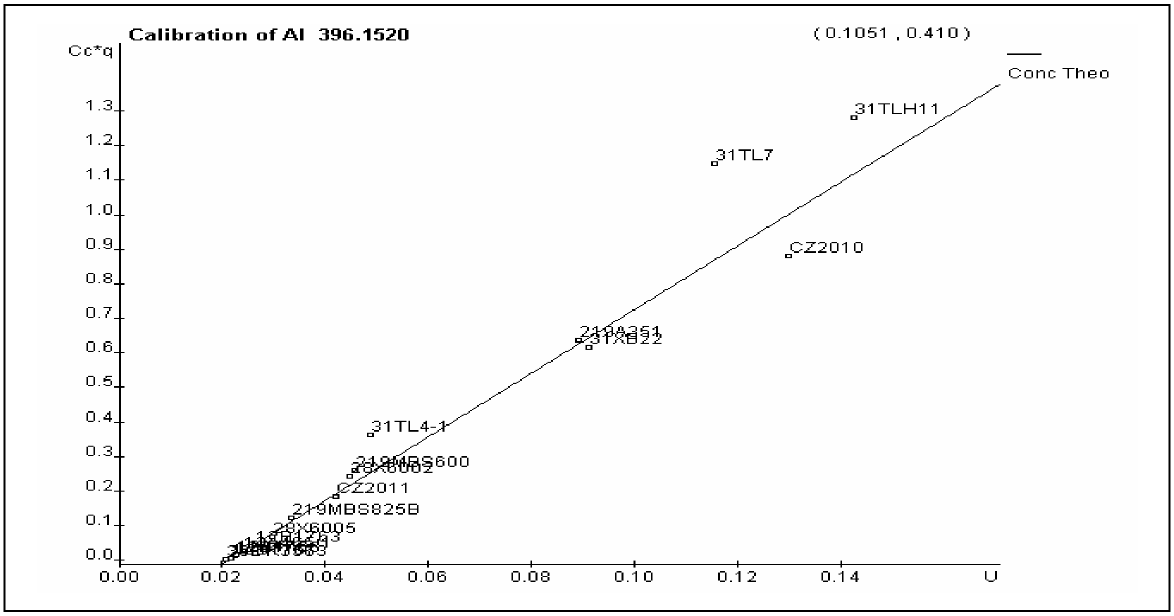


Figure 11. Detail of the calibration graph in figure 10, for aluminium in the concentration range 0-0.5 mass%.

3.4.3 Calibration graph for iron

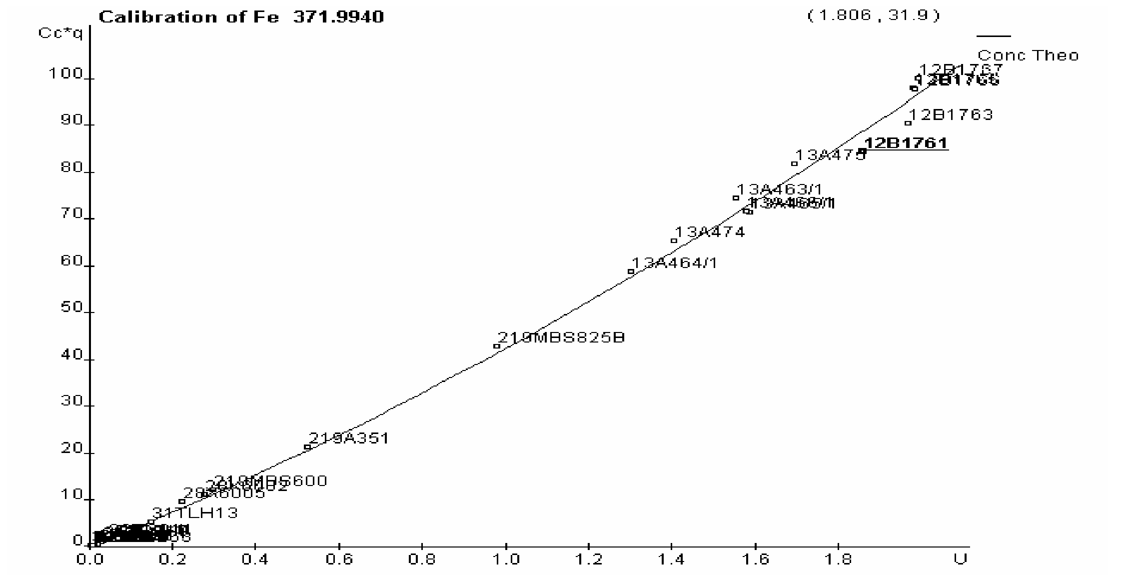


Figure 12. Calibration graph for the whole concentration range of iron in the calibration samples. Due to weak self-absorption of the Fe372 line, a non-linear calibration curve had to be fitted.

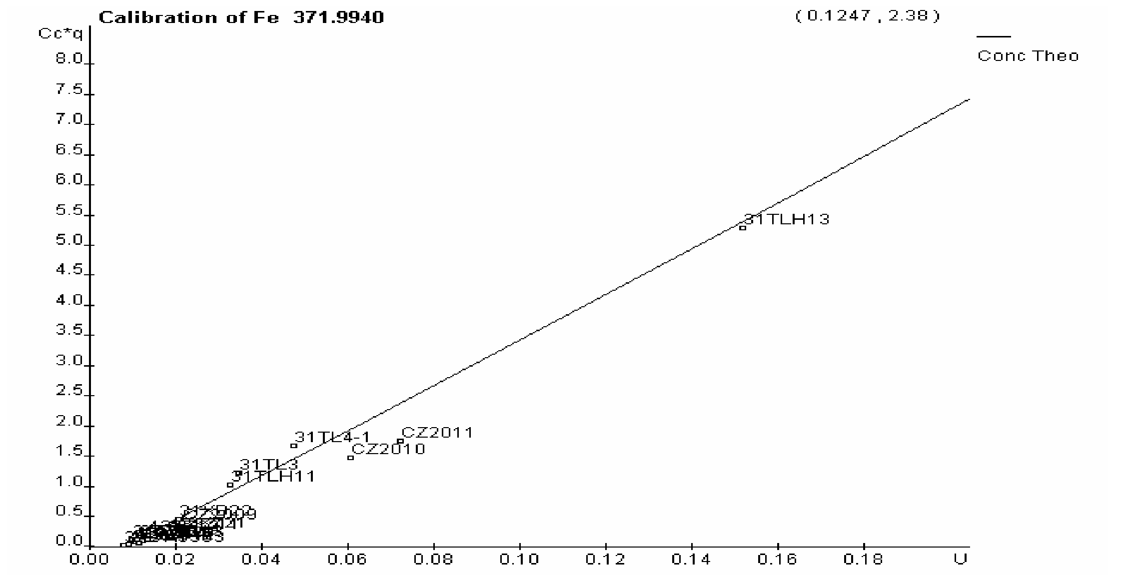


Figure 13. Detail of the calibration graph in figure 12, for iron in the concentration range 0-2.0 mass%.

3.4.4 Calibration graph for Ni

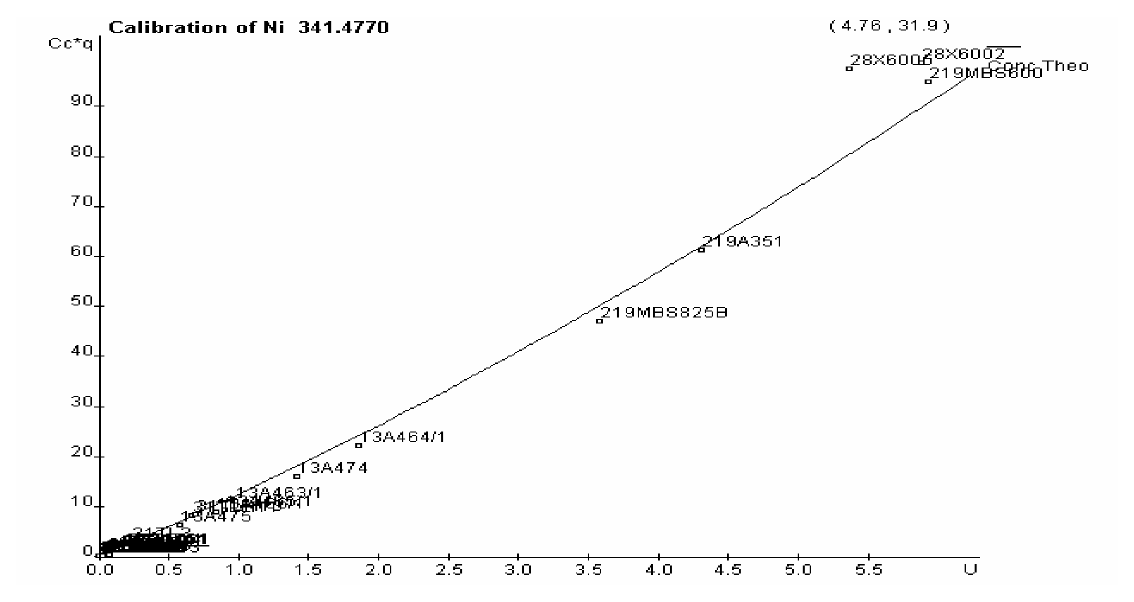


Figure 14. Calibration graph for the whole concentration range of nickel in the calibration samples. Due to weak self-absorption of the Ni341 line, a non-linear calibration curve had to be fitted.

3.4.5 Discussion

The most important calibration curves for this project were those for zinc, aluminium and iron. For aluminium and iron a reasonably good to excellent fit of the calibration data was obtained (figures 10-13). For zinc some problems were experienced. Figure 8 shows a clear separation between calibration points for the brasses and calibration points for the zinc-alloys. The fitted curve is rather arbitrary and one can use it to tune the results to some or even a large extent. Obviously this is not good practice. In figure 8 the curve basically connects the zero point (pure copper) with the 4.5 mass% aluminium in zinc point, to give reasonable results for the analysis of GI and GA. If the brass samples are excluded from the calibration, which is the obvious thing to do, considering the nature of the test samples, the slope of the best curve is allowed to change significantly and analysis results were completely out of range. This might indicate that there is a problem with the quality of some of the MBH zinc-alloys. When the CMI samples are included in the calibration a separation appears to occur between CMI zinc-alloys and MBH zinc-alloys (figure 9). This separation is much less pronounced in the aluminium calibration graph (figure 10-11). Although both the quality of some of the zinc-alloys and the use of samples with well over 95 mass% of zinc might be questionable, one also has to bear in mind that the zinc-alloys sputter very fast and that zinc is the major element. Errors in sputtering rates for zinc-alloys will cause large error bars in the calibration graph. This again emphasizes the importance of procedures for the accurate measurement of sputtering rates.

3.5 Compositional depth profiles

3.5.1 GI

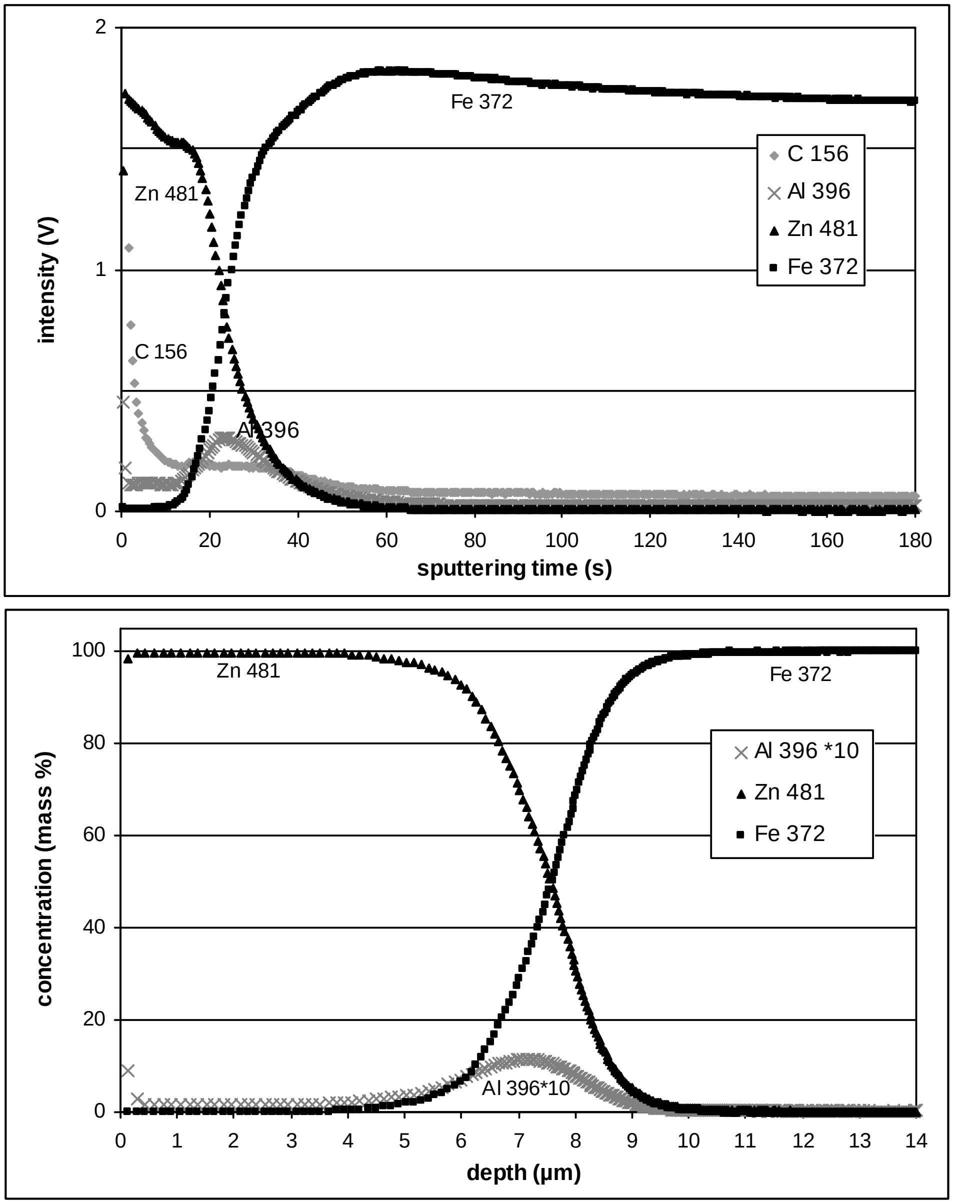


Figure 15. Qualitative depth profile (top) and corresponding compositional depth profile (bottom) of the hot dip galvanized sample GI. The mass% values for aluminium were multiplied by 10 for visibility.

3.5.2 GA

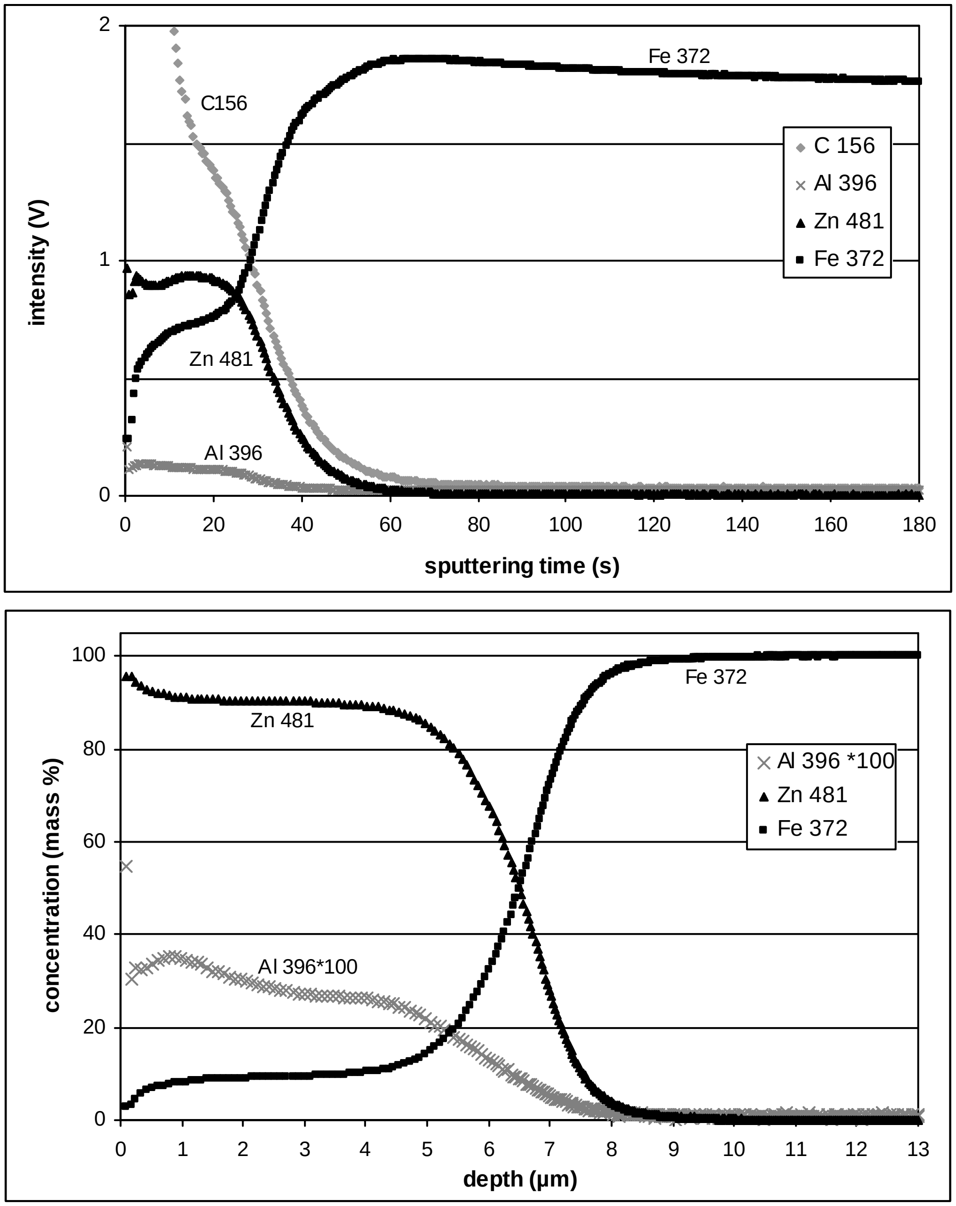


Figure 16. Qualitative depth profile (top) and corresponding compositional depth profile (bottom) of the galvannealed test sample GA. The mass% values for aluminium were multiplied by 100 for visibility.

3.5.3 Additional test sample 1 (“9025M”)

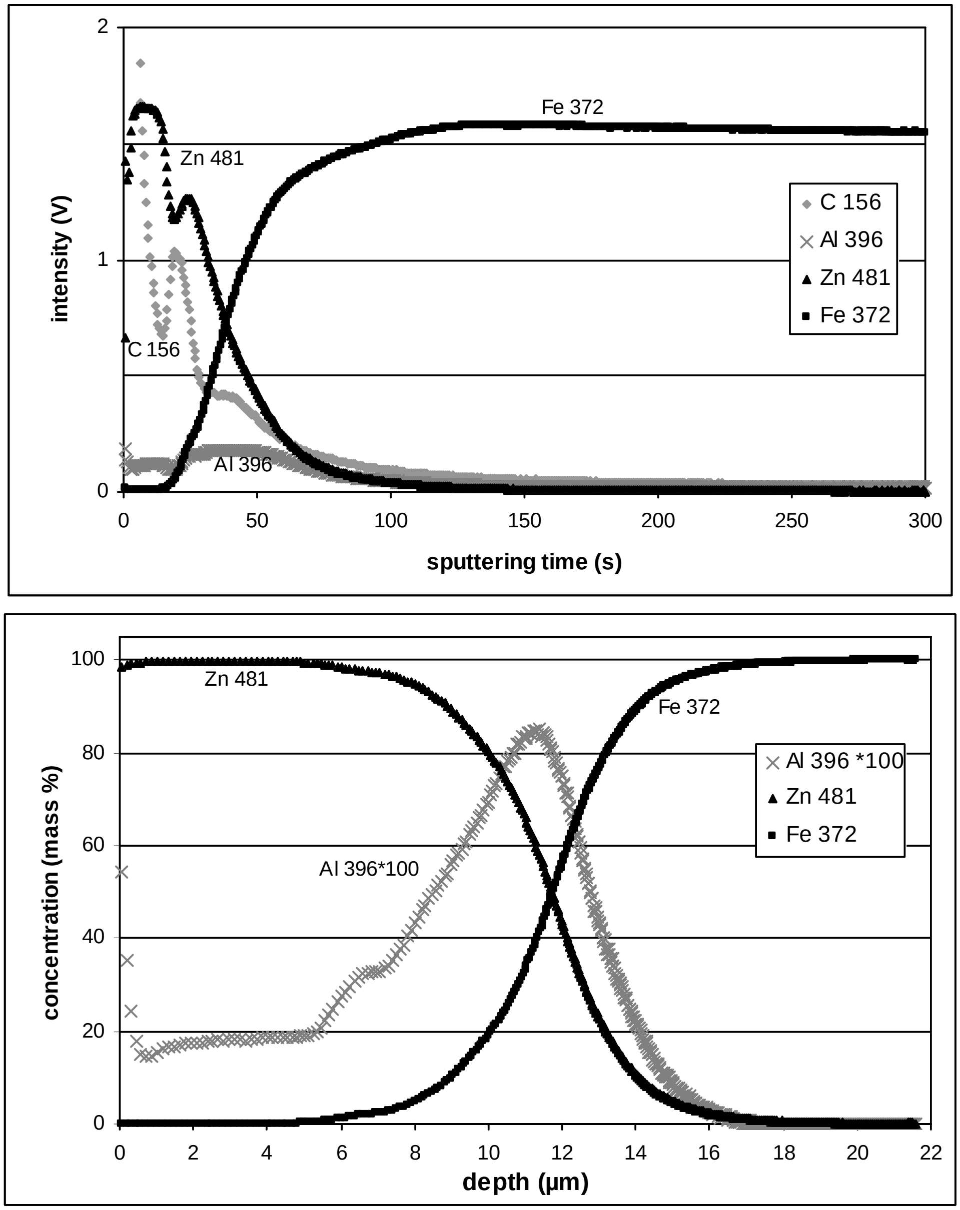


Figure 17. Qualitative depth profile (top) and compositional depth profile (bottom) of galvanized test sample 9025M. The mass% values for aluminium were multiplied by 100 for visibility.

3.5.4 Additional test sample 2 (“9100”)

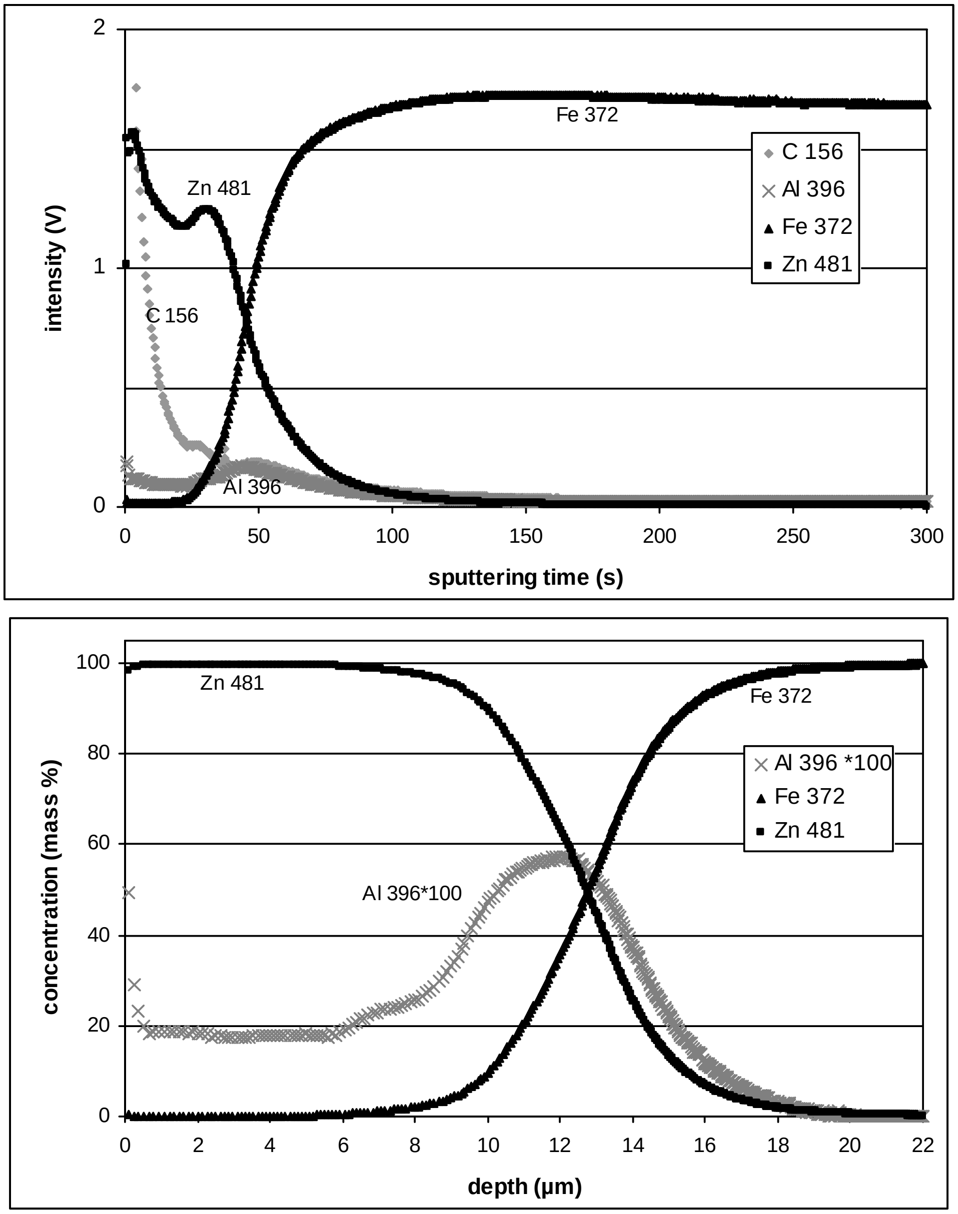


Figure 18. Qualitative depth profile (top) and compositional depth profile (bottom) of galvanized test sample 9100. The mass% values for aluminium were multiplied by 100 for visibility.

3.5.5 Additional test sample 3 (“galvannealed”)

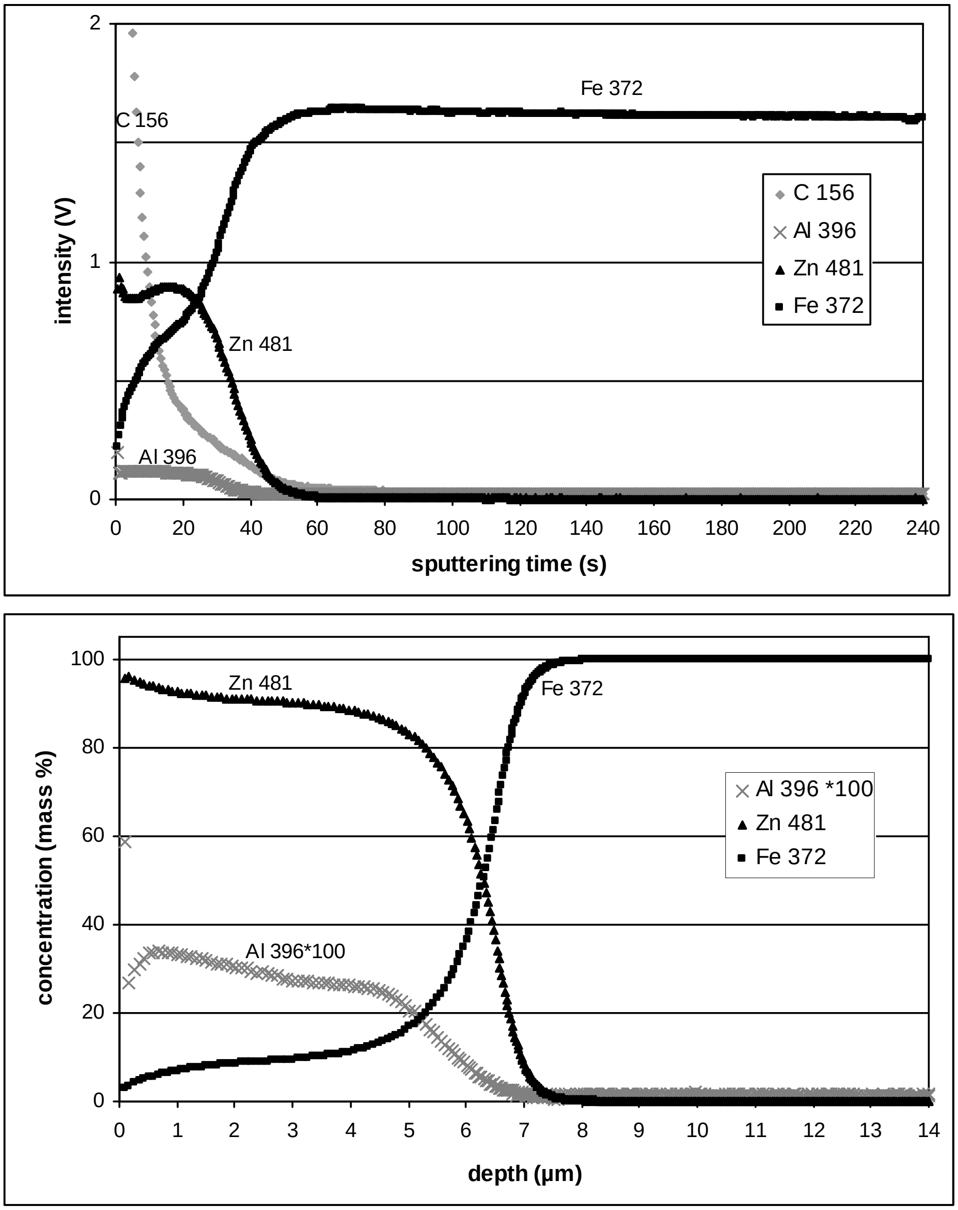


Figure 19. Qualitative depth profile (top) and compositional depth profile (bottom) of sample “galvannealed”. The mass% values for aluminium were multiplied by 100 for visibility.

3.5.6 Additional test sample 4 (“aluzinc”)

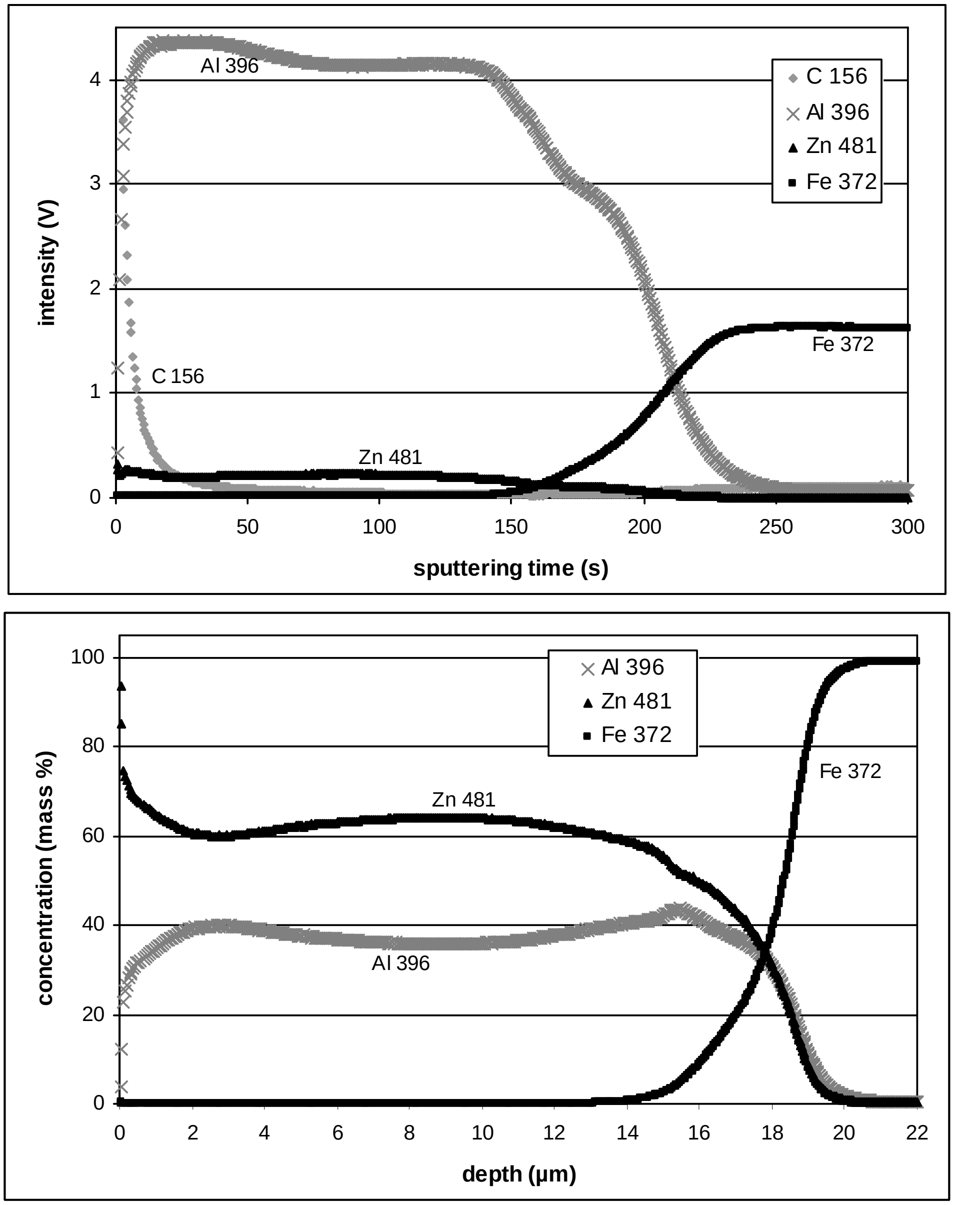


Figure 20. Qualitative depth profile (top) and compositional depth profile (bottom) of aluzinc test sample “aluzn”.

3.6 Thicknesses and compositions

Tables XI-XII summarize RF GD-OES results for coating thickness and total coating weight for all zinc-based coatings measured as test samples in the GAMeS project. Comparison is made with ICP results. For thickness and zinc-content ICP and GD agree within 10%. For aluminium the agreement between both techniques is not as good: differences up to 20% do occur for some samples; the differences are not systematic and cannot readily be understood. For low iron contents, GD values for iron are up to a factor of 6-7 higher than those obtained with ICP. This is problematic. It indicates that the integration interval for iron in the compositional depth profiles is too large. There is a need for better international procedures (cfr. §2.7).

Table XI. Thickness and total coating weight for Zn, Al and Fe for a variety of test samples.

		Thickness (µm)		**Zn (g/m²)**		**Al (g/m²)**		**Fe (g/m²)**	
		Average	SD	Average	SD	Average	SD	Average	SD
GI-Top	GD	8.3	0.4	57	3	0.30	0,01	0.46	0.03
	ICP-MS	7.5		53		0.34		0.25	
	ICP-OES			54		0.31		0.26	
GI-Bottom	GD	7.0	0.3	47.8	0.8	0.29	0.01	0.44	0.02
	ICP-MS	7.5		52.9		0.33		0.28	
	ICP-OES			54.0		0.31		0.26	
GA-Top	GD	6.8	0.3	43	2	0.12	0.01	4.69	0.04
	ICP-MS	6.5		40		0.11		5.50	
	ICP-OES			40		0.13		4.57	
GA-Bottom	GD	6.3	0.4	39	2	0.12	0.01	4.66	0.13
	ICP-MS	7.3		45		0.14		5.90	
	ICP-OES			40		0.13		4.57	

		Thickness (µm)		**Zn (g/m²)**		**Al (g/m²)**		**Fe (g/m²)**	
		Average	SD	Average	SD	Average	SD	Average	SD
8867-Mb-Top	GD	15.1		102		0.41		0.95	
ICP	ICP-MS	13.9		99		0.41		0.15	
8867-Mb-Bottom	GD	11.3		81		0.43		0.68	
ICP	ICP-MS	10.3		73		0.35		0.18	
8867-Lb-Top	GD	12.9	1.3	92	9	0.41	0.01	0.82	0.08
ICP	ICP-MS	12.4		88		0.34		0.14	
8867-Lb-Bottom	GD	10.2	0.8	71	5	0.36	0.02	0.72	0.03
ICP	ICP-MS	8.8		62		0.26		0.13	
8867-Rb-Top	GD	13.1	2.3	91	19	0.39	0.03	0.65	0.16
ICP	ICP-MS	11.9		85		0.39		0.16	
8867-Rb-Bottom	GD	9.50	0.01	68	1	0.39	0.02	0.68	0.15
ICP	ICP-MS	9.50		68		0.32		0.16	

Table XII. Thickness and total coating weight for Zn, Al and Fe for a variety of test samples.

		Thickness (µm)		**Zn (g/m^2)**		**Al (g/m^2)**		**Fe (g/m^2)**	
		Average	SD	Average	SD	Average	SD	Average	SD
9025-Mb-Top	GD	11.8	0.7	84	5	0.52	0.03	0.7	0.1
	ICP-MS	10.0		71		0,44		0.30	
9025-Mb-Bottom	GD	10.3	0.5	72	3	0.47	0.01	0.60	0.05
	ICP-MS	11.7		83		0.44		0.29	
9100-B-Top	GD	12.5	0.5	87	4	0.47	0.01	0.87	0.03
	ICP-MS	12.5		89		0.39		0.31	
9100-B-Bottom	GD	9.5	0.4	66	3	0.37	0.01	0.66	0.04
	ICP-MS	10.6		75		0.36		0.27	
9441-1E-Top	GD	19.6	1.2	138	8	0.61	0.02	1.11	0.07
9441-1E-Bottom	GD	13.6	1.2	92	9	0.45	0.04	1.15	0.07
9441-2E-Top	GD	21	4	145	26	0.57	0.04	1.2	0.2
9441-2E-Bottom	GD	20.6	0.2	141.4	0.7	0.55	0.03	1.41	0.09
AluZn-Top	GD	20	2	60	6	38	3	0.01	
AluZn-Bottom	GD	18	2	51	4	33	2	0.05	0.04

		Thickness (µm)		**Zn (g/m^2)**		**Al (g/m^2)**		**Fe (g/m^2)**	
		Average	SD	Average	SD	Average	SD	Average	SD
HDG-TKS	GD	8.2	0.3	56	2	0.31	0.01	0.57	0.02
	ICP-MS	7.8		55.5		0.39		0.40	
HDG-OCAS	GD	19	1	130	8	0.42	0.05	1.0	0.3
	ICP-MS	19		136		0.42		0.14	
HDG-OCAS + Pb	GD	79	1	531	9	0.14	0.01	35	2
	ICP-MS	81		575		0.16		27.0	
AluZink	GD	15.1	0.6	41	2	30.7	0.8	0.04	0.03
	ICP-MS	13.7		36.7		29.9		0.84	
Galvannealed	GD	6.5	0.4	41	3	0.12	0.01	4.9	0.2
	ICP-MS	5.3		33.6		0.16		4.3	

3.7 Interlaboratory comparison

The participants to the interlaboratory comparison are listed in Table XIII. Unfortunately, the data of 2 of the 15 participants could not be incorporated in this report, due to last minute technical problems. However, these data will be included in a separate report of the interlaboratory comparison that will be distributed to all participants. The results of the interlaboratory comparison are summarized in Table XIV and in Figures 21-23. The number with which each participant is identified in Table XIV is in no direct relation to the participants' position in Table XIII, in order to assure anonymity (as requested by 2 participants). Overall relative standard deviations for thickness, zinc and aluminium are 17%, 18% and 48%, respectively. Note that two participants reported extreme values for aluminium, a high and a low, respectively. Only half of the participants reported a value for iron and the relative standard deviation for this element is huge. This again underlines the need for a procedure for integration.

Table XIII. Participants to the interlaboratory comparison.

Company /Institute	Country	Equipment	Source
Aceralia	Spain	Leco 850	DC
BAM	Germany	Leco SDP 750	DC
Certech	Belgium	JY10000RF	RF
CRM	Belgium	Leco GDS 750A	DC
FQZ Brandenburg	Germany	Leco GDS 750	DC
EMPA	Switzerland	JY5000RF	RF
IFW Dresden	Germany	Spectruma GDA750	DC
Jobin-Yvon	France	JY5000RF	RF
Leco	Czech Republic	Leco GDS 750A	DC
Ocas	Belgium	Spectruma GDA 750	DC
Robert Bosch Bamberg	Germany	Spectruma GDA750	DC
Salzgitter	Germany	Spectruma 1000	DC
SIMR	Sweden	Leco 750	DC
University of West Bohemia	Czech Republic	Leco SDP 750A	DC
VITO	Belgium	JY5000RF	RF

Table XIV. Results of the interlaboratory comparison on GI.

Participant	Thickness (µm)		Zn (g/m²)		Al (g/m²)		Fe (g/m²)	
	Average	SD	Average	SD	Average	SD	Average	SD
1	7.38	0.22	52.5	1.3	0.39	0.01	0.16	0.01
2	7.57	0.49	48.6	3.4	0.28	0.01	5.39	0.31
3								
4	6.77	0.15	46.8	0.9	0.020	0.004	0.001	
5								
6	5.75		40.3	2.2	0.26	0.01		
7	8.28	0.41	57.8	3.0	0.25	0.01		
8	11.38	0.86	78.3	5.8	0.42	0.01		
9	7.87	0.42	54.3	2.5	0.32	0.01		
10	8.26	0.26	56.9	1.6	0.25	0.01		
11	7.58	0.87	49.1	5.8	0.22	0.02	4.83	0.40
12	8.25	0.33	56.8	3.0	0.30	0.01	0.46	0.03
13	10.08	0.23	70.2	1.4	0.34	0.01	1.31	0.15
14	8.66	0.32	57.8	1.5	0.70	0.01		
15	8.88	0.03	57.6	0.1	0.23	0.03	0.32	0.06
AVERAGE	**8.2**	**1.4**	**56**	**10**	**0.31**	**0.15**	**1.8**	**2.3**
ICP-MS	7.5		52.9		0.34		0.25	
ICP-OES			54.0		0.31		0.26	

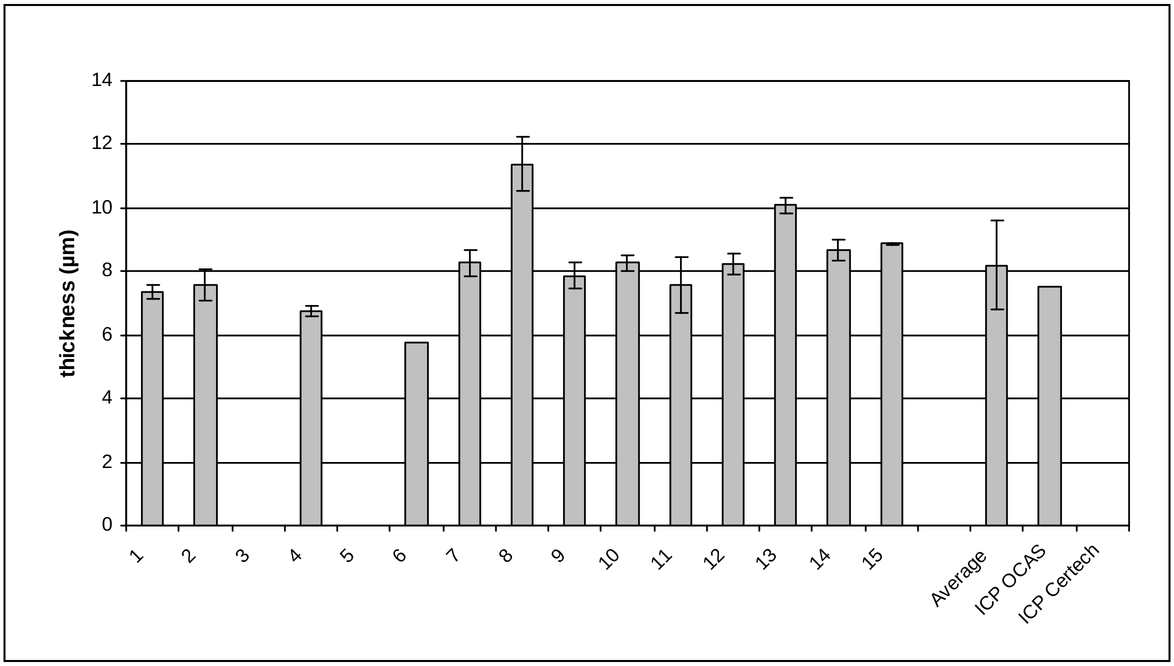


Figure 21. Interlaboratory comparison. Results for thickness of GI, with standard deviation.

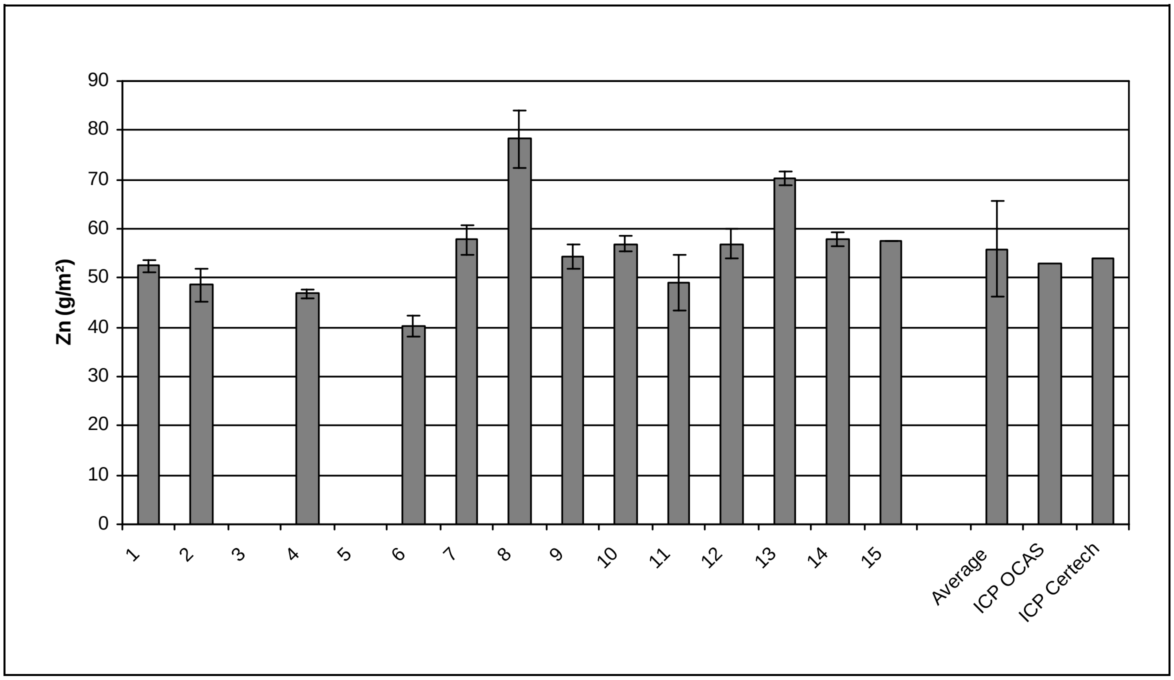


Figure 22. Interlaboratory comparison. Results for total zinc in GI, with standard deviation.

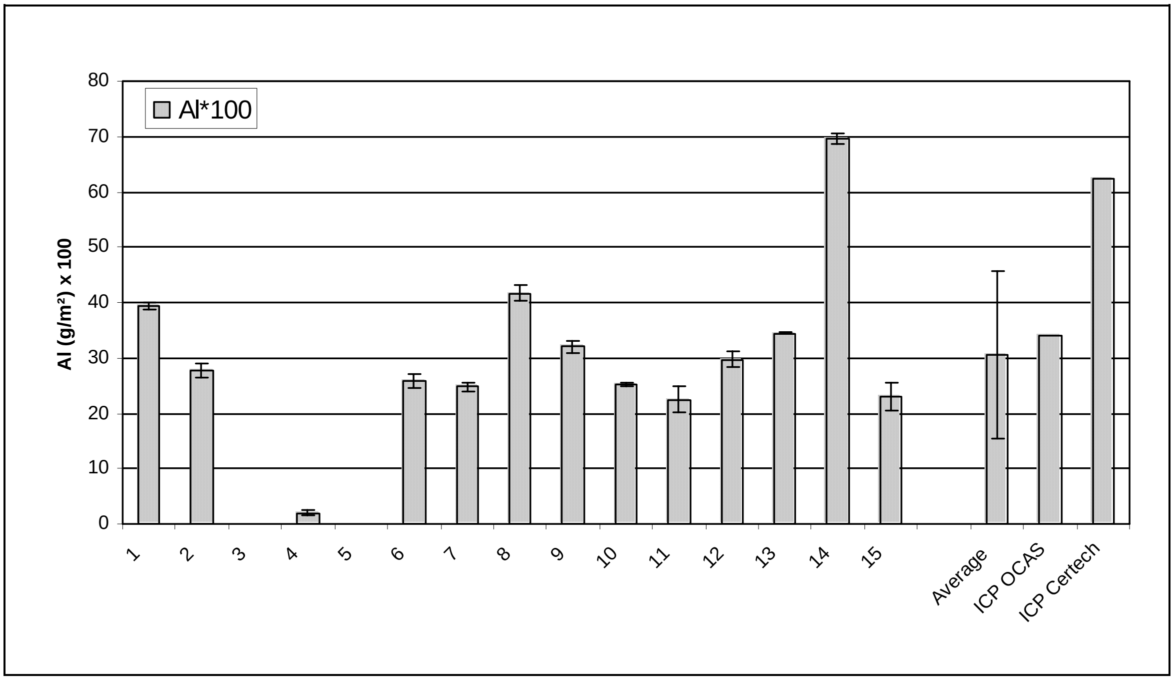


Figure 23. Interlaboratory comparison. Results for aluminium in GI, with standard deviation.

4 DISTRIBUTION AND VALORIZATION

Important results of the GAMeS project between Vito and Certech are:

a) An experimental procedure complementary to the ISO-standard under preparation, which can assist the implementation of this standard. The procedure will be distributed through this report and through a Vito-report based on this report.

b) Experience with the application of RF GD-OES for determining thickness and composition of zinc-based coatings on steel. Expertise and instrumentation of Certech and Vito are available to third parties, for contract work.

c) Awareness of the need for a procedure for measuring crater depths with a profilometer. Even the best standard for GD does not make any sense when crater depths and hence values for the relative sputtering rates cannot be measured correctly. Our results were presented at a meeting of Jobin-Yvon GD users, in the presence of an international expert and member of the ISO/TC201.

d) Awareness of the fact that a relative sputtering rate of a calibration sample can vary significantly and that these variations are not only due to errors in measuring the crater depth. The data were discussed with an international expert in the field and with a Belgian industrial GD user. The results were also presented at a meeting of Jobin-Yvon GD users. More work will be done to substantiate and publish the findings briefly discussed in this report.

e) Awareness of the fact that many European labs are ready to apply GD-OES to zinc-based coatings on steel, but that problems exist on the level of calibration, as well as on the level of integration of the compositional profiles. The results of our interlaboratory comparison will be reported to all participants and discussed with active members of the ISO/TC 201.

f) Know-how for the application of RF GD-OES in general. RF GD-OES is being incorporated in the strategic research of Vito as a depth profiling tool for fast diagnostics of coatings.

5 BALANCE AND PERSPECTIVES

This report describes an experimental procedure for measuring thickness and composition of zinc-based coatings on steel using RF GD-OES, as developed in the GAMeS project. The procedure was applied to industrial zinc-based coatings. The results were satisfactory, but important potential sources of error were identified. To our opinion GAMeS was important on two levels:

a) Belgian level. Two Belgian institutes, Vito and Certech, have collaborated intensely during the project and have gained extremely valuable experience. They have shared this experience with Ocas/Arcelor, with which they still have regular contacts and exchange of data on a scientific basis. They will be offering their know-how and instrumentation as a service to third parties (mainly Belgian industry, incl. SMEs). They have made Belgium a known and respected player in Europe in the field of GD-OES. It is hoped that Belgium can play a part in the development of an ISO-standard for the analysis of thin coatings with GD-OES.

b) European and international level. Our results have highlighted a number of problems on the level of relative sputtering rates, which are of importance for the whole GD-OES community. It is expected that our results will push 1) a procedure for the measurement of crater depths and 2) a systematic investigation of all parameters that can influence relative sputtering rates. Until now relative sputtering rates were assumed to be largely independent of analysis conditions and thus exchangeable between users.

ACKNOWLEDGEMENTS

The authors are indebted to the Belgian Science Policy, for financial support under contract no. NM/67/21; to Chris Xhoffer (Ocas, Belgium) for providing test samples and for enthusiastically sharing results and experiences; to Richard (Dick) Payling (Jobin-Yvon, France) for lots of practical information and theoretical background; to Arne Bengtson (SIMR, Sweden) for information and challenging statements. Dick and Arne are also acknowledged for continuously pushing the boundaries of GD-OES.

REFERENCES

Bengtson Arne, Hänström Sofia, Lo Piccolo Eugenio, Zacchetti Nicoletta, Meilland Raymond, Hocquaux Hubert, 1999, Surf. Interface Anal. **27**, 743-752.

Payling Richard, 1998, Spectroscopy **13**, 36-44.

Payling Richard, Jones Delwyn, Bengtson Arne (eds.), 1997, *Glow Discharge Optical Emission Spectrometry*, Wiley, Chichester.

Payling Richard, Larkins Peter, 2000, Optical *Emission Lines of the Elements*, Wiley, Chichester.

Uitgegeven in 2005 door het Federaal Wetenschapsbeleid

FEDERAAL
WETENSCHAPSBELEID

Wetenschapsstraat 8 ▪ B-1000 BRUSSEL
Tel. 02 238 34 11 ▪ Fax 02 230 59 12
www.belspo.be