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20 YEARS 1819-2019 HORIBA JOBIN YVON

XRF

Fast, easy and safe control of Zn-Ni galvanization baths with MESA-50, a portable EDXRF

Application Note

Metallurgy XRF21

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The XRF technique is used for elemental analysis of solids and even liquids. Thanks to dedicated sample cells, basic solutions can be analyzed by this technique. The electrolytic baths follow-up is an applicative example using the MESA-50. This specific example shows the ability of this instrument to characterize the degradation of Zn-Ni galvanization baths. This kind of electro deposition is used to substitute for Cd deposits which are very efficient corrosion protection, but are toxic for the environment.

Keywords: EDXRF, Zn-Ni electrolytic bath, galvanization bath follow-up, elemental analysis, basic solutions analysis

Introduction

For decades, cadmium has been employed as a robust and versatile metallic coating. When plated onto steel, cast iron, malleable iron, copper, and powdered metal, it functions as a «sacrificial coating,» corroding before the substrate material[1]. It has been largely used in electrical, electronic, aerospace, mining, offshore, automotive and defense industries. Despite remarkable properties, the main drawback of cadmium is its high toxicity that led to drastically reduce its use. So, its substitution by other coatings is a subject of great interest for many years.

One alternative coating is Zn-Ni alloy plating which is an efficient, economical coating, with minimal environmental impact. It could be used, for example, in the automotive industry, when corrosion protection is required, and because the alloy is superior to standard zinc plating[2]. A Zn-Ni plating containing between 12 to 15% of nickel behaves similar to cadmium plating[3].

The ASTM 2417 and ASTM B841 describe the requirements for electro deposition of a zinc-nickel alloy and the properties of the deposit.

As these alloys are deposited by galvanization processes, the bath concentrations are of great importance for the final composition of the plating. Therefore, a regular check of Zn and Ni concentrations is needed to ensure good properties of the final coating. One difficulty of this determination is that these baths are highly alkaline.

In this application note, we have used the MESA-50, a portable EDXRF instrument, as an easy, fast and safe way to control the Zn and Ni concentrations.

Instrument description and methodology

The MESA-50 is an EDXRF (Energy Dispersive X-Ray Fluorescence) instrument from HORIBA. The principle of X-Ray fluorescence is quickly described in **figure 1**:

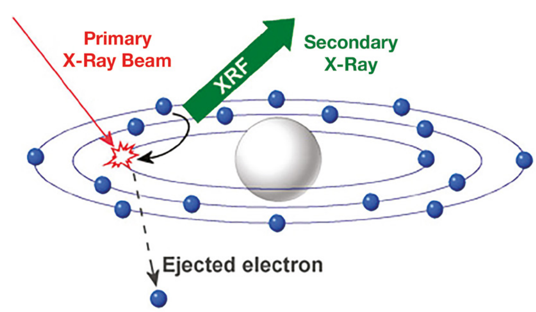


Figure 1 : Principle of secondary X Ray emission

Figure 2 : MESA 50, X Ray fluorescence

A primary X-Ray (external stimulation in **figure 1**) kicks out an electron from an inner shell. An electron from an upper shell fills the gap by releasing the energy difference from the two levels as a secondary X-Ray. Depending on initial and final shells concerned by this phenomenon, the emitted X-rays have different names: Kα, Kβ, Lα, etc. As this difference of energy is characteristic of a specific transition in one specific atom, the EDXRF will provide the nature of this atom.

Furthermore, as the quantity of X-rays emitted at one specific energy is linked to the concentration of this element, a quantitative analysis is even possible. However, due to inter-element effects, this quantification needs calibration by using standards or FPM (fundamental parameter method).

In the EDXRF, the detector is energy dispersive. On the MESA-50, a SDD (Silicon Drift Detector) is used. It allows high count rate with good energy resolution. Furthermore, this kind of detector uses the Peltier effect to cool down and doesn't require liquid nitrogen.

Based on its long experience in X-Ray analysis, HORIBA developed the MESA-50, a very compact instrument that brings together portability and safety. Moreover, due to its background in the petroleum industry, HORIBA has developed specific sample holders for liquids. The anticathode used in the X-Ray tube is made of Pd.

Measurements and results

The aim of these analyses was to monitor the Zn and Ni concentration of the alkaline galvanization bath for electro deposition of Zn-Ni on steel.

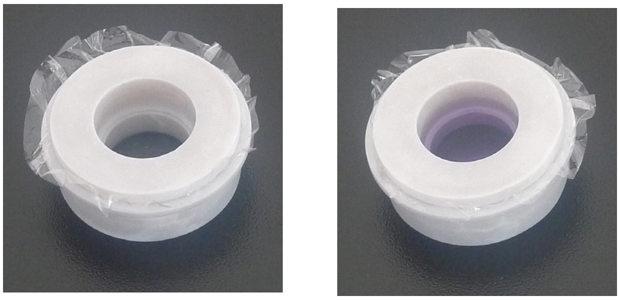
The first step consisted of making calibration curves with solutions of known concentrations of Zn and Ni. Then, two other known solutions, not used for the calibration, were measured to check the validity of the curve. Finally, one real sample coming from a used galvanization bath was tested.

The different solutions used for the calibration were obtained by mixing of alkaline solutions of Zn, Ni, soda and water. Soda was added in order to reach the same level of 130g/l in all the final solutions. The table below gives the respective Zn and Ni concentrations:

Table 1: Standard solutions concentrations

Solution	1	2	3	4	5
Zinc concentration (g/l)	4.989	7.021	10.205	12.016	15.107
Nickel concentration (g/l)	2.507	2.011	0.498	1.051	1.502

About 5ml of these solutions were poured in a specific sample cell, particularly well designed for liquids. As this cell is made of Teflon, it is alkaline resistant.



Empty *Filled with the solution*

Figure 3 : Sample Cell

After warming up the instrument, the following conditions were set up:

Table 2 : Measurement conditions

Parameter	Value
Acceleration voltage (kV)	50
Current intensity (mA)	auto
Collimator (mm)	7
Processing time	P2
Measurement time (s)	200
Filter	middle

After measuring the five solutions, a linear regression gave the following curves:

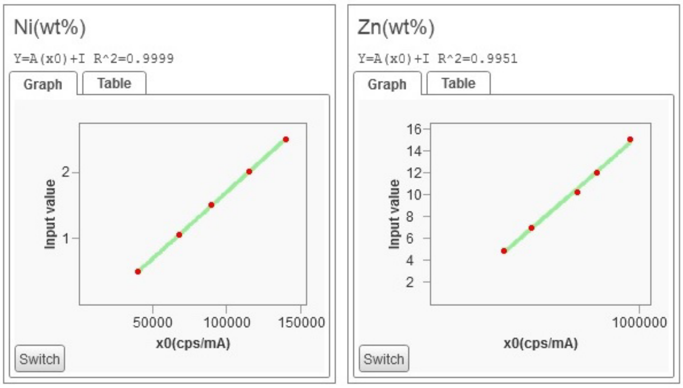


Figure 4 : Sample Calibration curves

These two curves showed a good regression coefficient by using a linear model. This is a very good indication that EDXRF is a suitable method for this kind of application.

Two known synthetic solutions were analysed to validate the calibration:

Table 3 : Expected and obtained results

Solution name	Et1	Et2
Zinc concentration (g/l)		
Expected	10.006	7.516
Measured	9.932	7.596
3 sigma	0.010	0.009
Nickel concentration (g/l)		
Expected	2.006	1.503
Measured	2.001	1.500
3 sigma	0.005	0.005

The difference between expected and obtained results was no more than 1%. Furthermore, the standard deviation (3σ) was also excellent.

Finally, an unknown solution coming from a used galvanization bath was analyzed:

Table 4 : Results of unknown sample

Solution name	X
Zinc concentration (g/l)	6.580
3 sigma	0.008
Nickel concentration (g/l)	1.062
3 sigma	0.004

These results fall inside the calibrated ranges for both elements. That confirms that the calibration curves are suitable for the concentration range that has to be followed. Furthermore, the standard deviation was still very good, even on a production sample.

Eventually, if this kind of measurement needs to be used on a production line, the analysis can be simplified. Indeed, the MESA-50 software makes the registration of a recipe possible, including the measurement conditions and the quantification parameters. A button can be assigned to this task. The operator will only have to push this button after preparing and placing the cell in the instrument to obtain the results. Finally, high and low limits with uncertainty can be stated, and clear information (Good or Non Good) are provided with the final results.

Conclusion

Due to its toxicity, anticorrosive treatments using Cd are about to be completely prohibited, so alternative treatments are widely studied and used. One of them is Zn-Ni coating deposited by electro deposition. For the plating quality and properties, the concentration of the galvanization baths needs to be controlled throughout its life time.

If methods like ICP-OES could be used, the high concentration level requires dilutions steps which are time consuming and can induce errors. In this application note, a direct method with no dilution was developed using the MESA-50, an EDXRF instrument.

Two calibration curves, both for Ni and Zn, were built with synthetic solutions. These curves were validated by testing two other synthetic solutions. Finally, a solution from a used bath has completed the validation by showing that these curves were suitable to check the targeted concentrations.

This method can be extended to any galvanization bath control. Furthermore, the ability of the MESA-50 to assemble all the operations, measurement parameters, quantification and judgment, using a single button, make it ideal for controlling the production, and for making the decision whether the bath has to be replace or not.

References:

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