Direct Determination of Phosphorus Content in Electroless Nickel Plating Using X-ray Fluorescence (XRF) Spectroscopy

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Abstract
Electroless plating processes are popular because of their performance, reliability and cost effectiveness. The process combines unique deposit properties such as uniform plating build up regardless of geometry, excellent corrosion resistance, superior hardness and wear and the ability to plate on non-conducting materials. The most commonly used electroless plating process is Electroless Nickel (EN) plating using nickel phosphorus baths. The phosphorus content plays a fundamental role in all physical properties of the deposit. It is, therefore, critical to control the phosphorus content within a relatively tight range. X-ray fluorescence is an excellent method to not only measure plating thickness but also weight percent elemental composition of coatings. Previously, it was only possible to measure plated phosphorus content on steel substrates. New developments in XRF instrument hardware and software have extended the measurement application of electroless plating processes to nearly any substrate. The simultaneous measurement of thickness and composition is critical.

1 Introduction

Phosphorus, the concentration of which significantly influences the mechanical and magnetic properties of the coating, is incorporated during electroless or chemical nickel deposition [1]. For this reason, measurement of the phosphorus content has been an important issue ever since electroless nickel deposition methods were introduced. As an alternative to the established wet-chemical methods, during which the coating is dissolved and therefore destroyed, non-destructive and simpler methods are desired. XRF provides such a non-destructive test method, where utilisation of the characteristic emissions of P-K radiation can provide direct measurement of the Phosphorus content. Energy dispersive X-ray spectrometry (EDX) utilizing electrons for excitation in electron probe micro analysis (EPMA) or charged particles in particle induced X-ray emission (PIXE) have been analytical techniques used for determining phosphorous content for a long time. While the first method is integrated into many electron microscopes, the latter requires an accelerator. High vacuum is required in either case.In X-ray fluorescence analysis (XRF), an incident X-ray beam is used as the excitation source. This is typically and X-ray tube. For all three described excitation methods the resulting fluorescent signal is interpreted in the Energy Dispersive X-ray spectrometer. XRF is well established in process control instrumentation, especially in the electroplating industry and has been used for decades to determine both coating thicknesses and coating compositions [2]. However, it is impossible to determine the thickness of a nickel/phosphorus coating using X-ray fluorescence without knowing the phosphorus content. The phosphorus content in the nickel changes the coating density and attenuates the other fluoresced components used in the measurement process. The phosphorus concentration of a nickel/phosphorus alloy coating has been obtained indirectly, by measuring the attenuation of base material fluorescence as described in section 2.2. This method, without directly measuring the P-K signal was described in 1989 [3] and is integrated in some instrument manufacturers' application software. Reliable direct measurement of the P-K radiation has been limited in conventional, air path XRF instruments by detector technology , i.e. proportional counter tubes or Peltier-cooled Si-PIN diodes. The low-energy P-K radiation can either not be detected or insufficiently detected. Nonetheless, this widely used technique has great advantages; it requires no vacuum and operation of the instruments is simple enough that it can be used on the plating floor. Now with the recently available SDDs (Si Drift Detectors) direct measurement of P-K radiation in air is possible and, therefore, extends the application to base materials other than Fe, such as, Al or plastics.

The following discusses this in greater detail.

2 Direct and Indirect Determination of the Phosphorus Content
2.1 The Coating Model

In the coating model depicted below (*Figure 1*), the nickel/phosphorus coating is viewed as a plane parallel alloy coating that contains only the elements nickel and phosphorus with a homogeneous element distribution. Typically, organic and/or metallic stabilisers (i.e. lead) in trace concentration ranges can be neglected. If lead-free stabilisers are present in concentrations that affect the XRF analysis, they can be taken into account as an additional alloy element or elements.
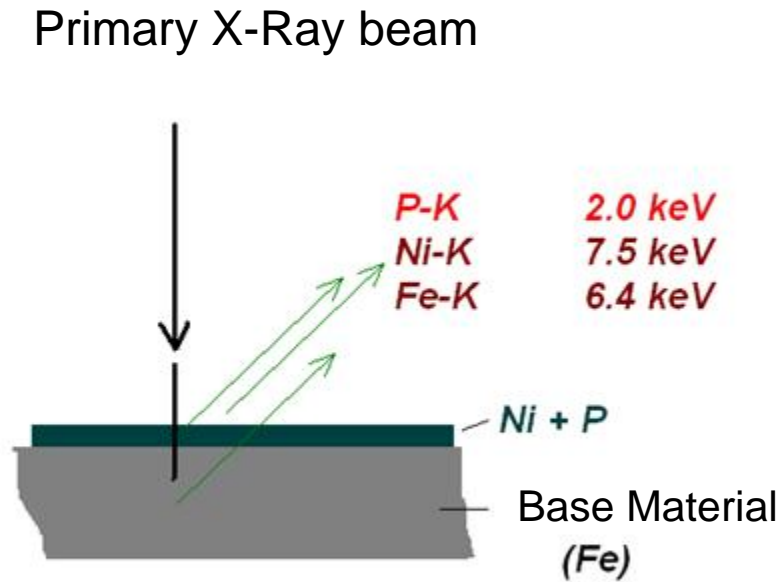

Figure 1: Coating model and schematic of the fluorescence excitation.

The radiation components relevant for XRF are Ni-K (7.5 keV and 8.3 keV) and P-K (2.0 keV), as well as, the fluoresced components of the substrate material, which in *Figure 1,* is iron (6.4 keV and 7.1 keV).

2.2 Indirect Phosphorus Measurement
The indirect determination of the phosphorus content [3] uses only the easily measurable radiation components of nickel and the substrate material iron. This approached is used with proportional counter tube based instruments, because a proportional counter tube is not able to detect the P-K radiation. *Figure 2* shows related model calculations for the conditions of a Fischerscope® X-Ray XULM proportional counter system. Displayed are the modelled spectra for a 5 μm thick nickel/phosphorus coating on iron, with the phosphorus content varying between 0% and 15%.

One notices a clear dependence of the Ni and Fe intensity with respect to the phosphorus content. The physical reason is the absorption effect of the element phosphorus on both the Fe-K and the Ni-K radiation. So, there is a well-defined correlation between the thickness of the nickel/phosphorus coating and its phosphorus content as the unknown measurement variables and the intensities of Fe-K and Ni-K radiation that can be measured with a proportional counter tube. For a constant thickness, more phosphorus reduces the Ni-K intensity relative to the Fe-K intensity, because the absorption by phosphorus is less for iron than nickel. The evaluation software *WinFTM* [2] processes this information and computes the thickness and the composition of the coating from the measured spectrum. *Table 1* shows the results obtained from the measurement of a flat NiP/Fe reference sample. The measuring application was not calibrated (standards-free analysis). The small deviation from the nominal value indicates that the model underlying the evaluation is quite good. Even more important is the good precision of 0.25% for the phosphorus concentration. However, it is apparent that the total measurement uncertainty increases due to systematic uncertainty (*Section 3*).
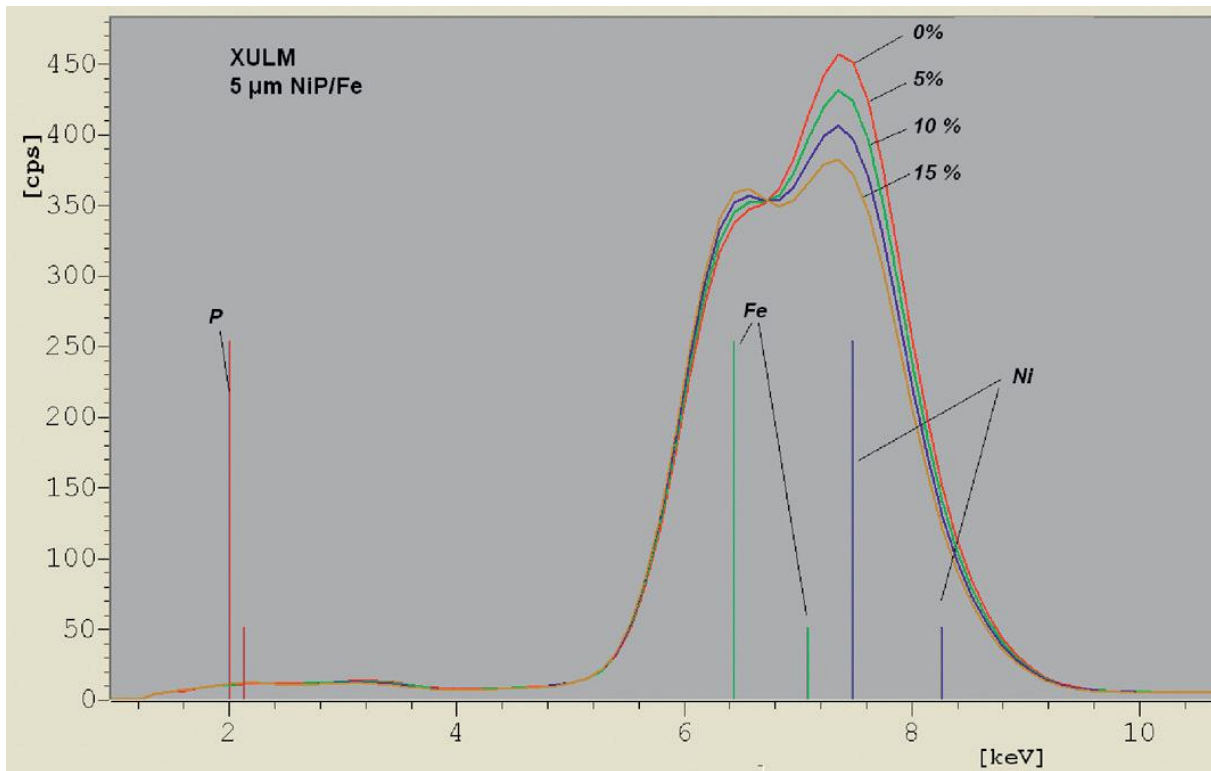
Figure 2: Computed spectra for a 5 µm thick nickel/phosphorus coating on iron, applicable for the measurement conditions of a Fischerscope® X-Ray XULM, 50 kV, Ni-filter. The detector is an Xe-filled proportional counter tube. It is not possible to evaluate the P-K peak at 2 keV with this type of detector.

An error due to possible distance variations must be considered as part of the random measurement uncertainty. A shift in the measurement distance results in a change in intensity of all spectral components and in particular, in erroneous %P readings *Figure 3* illustrates this based on the specimen from *Table 1*.

In general the uncertainty of the measuring distance setting z is better than 50 µm, such that, the resulting uncertainty in determining the concentration is about 0.2% phosphorus. If one further considers that a positioning uncertainty also occurs during calibration, then this error source must be estimated at about 0.3% phosphorus. This is the same magnitude as the precision itself. Other sources of error (influence of curvature and tilt of the specimen surface) during the indirect measurement of NiP/Fe can also contribute to the total error.

One aspect of the distance dependence often surprises the user: Newer model instruments with high-resolution semiconductor detectors are not at all suited for this approach, because the distances between sample and detector are significantly smaller. For this reason, distance uncertainties of the same magnitude, i.e. <50 µm, are significantly more serious (by a factor of 2 to 3!) than with proportional counter tube instruments. This must be taken into account when evaluating spectra with a direct phosphorus analysis (*Section 2.3*).

Table 1: Measurement documentation for the standards-free thickness and composition determination of a NiP/Fe reference sample (14.3 μm, 9.3% P); Measurement under repeatability conditions

Fischerscope® XRAY XDLM-C4
Application: 216 / NiP/Fe

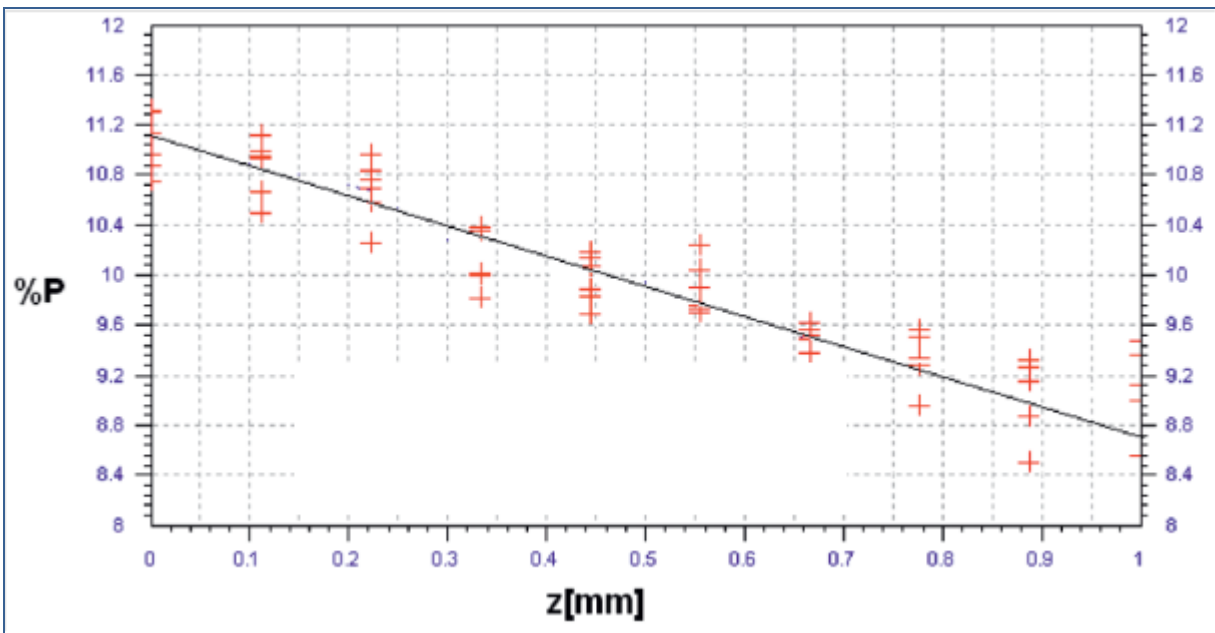| Individual results		
n = 1	P Ni1 = 13.0 μm	P 1 = 9.45 %
n = 2	P Ni1 = 12.9 μm	P 1 = 9.23 %
n = 3	P Ni1 = 13.1 μm	P 1 = 9.63 %
...		
n = 10	P Ni1 = 13.1 μm	P 1 = 9.52 %
Mean value	12.96 μm	9.395 %P
Standard deviation	0.099 μm	0.25 %P
Number of measurements	10	10
Lowest reading	12.8 μm	8.98 %P
Highest reading	13.1 μm	9.83 %P
Measuring time	30 s	

Figure 3: Measured distance dependence of the %P measurement using a Fischerscope® X-Ray XDLM-C4 for the sample from Table 1; the correct measuring distance is z = 0.5, the measurements are repeated several times, the scatter provides a measure for the random (statistical) measurement error.

2.3 Direct Phosphorus Measurement (analysis of P-K- Peak)

Si Drift Detectors (SDDs) can achieve today what was impossible with even Si-PIN detectors of the last decade. The P-K radiation component can be detected reliably: *Figure 4* graphically illustrates the measurement effect. Samples with different phosphorus contents show P-K peaks of different magnitudes. Their intensities are (nearly) proportional to the phosphorus content.
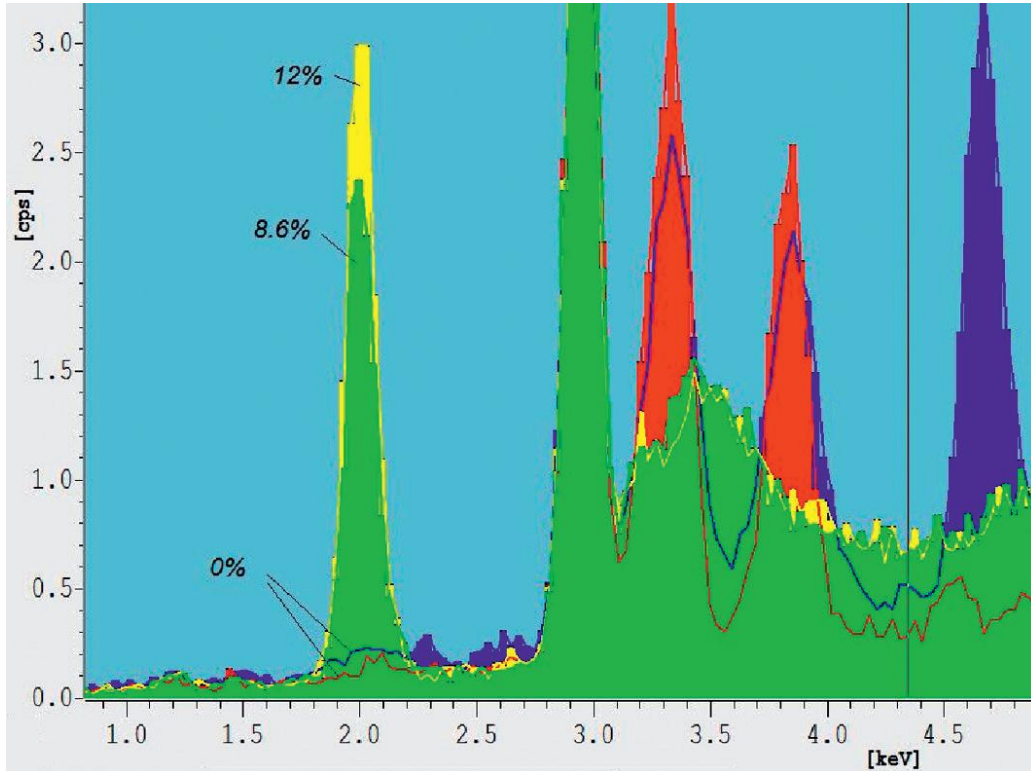

Figure 4: Fluorescence spectra of nickel/phosphorus coatings with different phosphorus content: the intensity of the P-K peak directly represents the phosphorus concentration.

The energy of the characteristic P-K radiation is only 2 keV. Due to the very critical dependence of the absorption coefficient on the photon energy, the information depth is just under 1 μm (*Figure 5*).
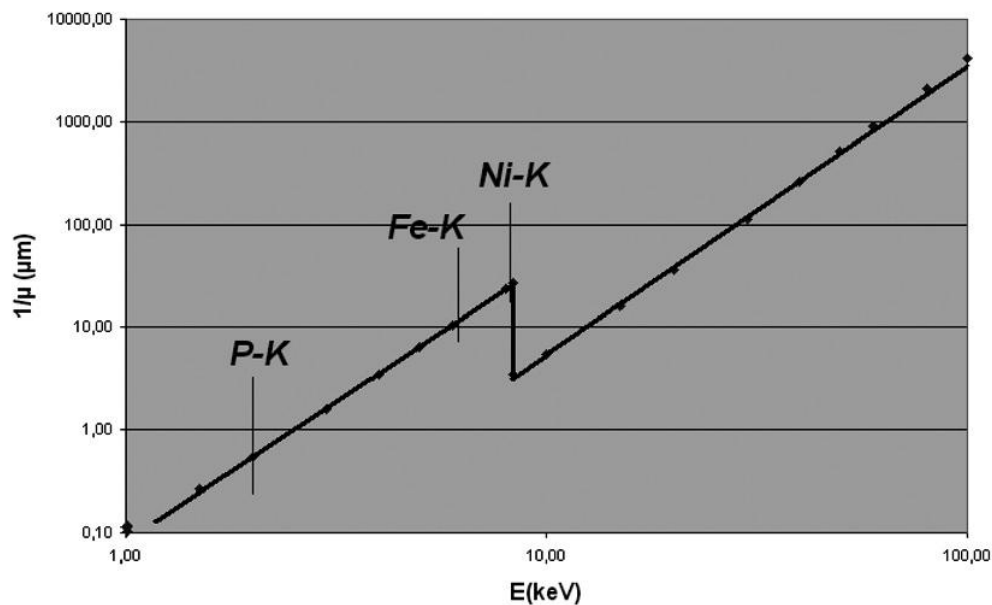
Figure 5: Information depth dependence (reciprocal linear attenuation coefficient) for the element nickel.

As shown in *Figure 6,* the spectral signal of the phosphorus is not very large. For commonly used excitation conditions (W-Anode, 50 kV, 10 μm Ni-Filter) and a typical sample of about 10% P, the P-K peak is 2000 times smaller than that of Ni-K. This combined with a rather poor signal/background ratio of only 2 provides unfavourable conditions for routine analyses. The signal/background ratio, which is so important for the measurement sensitivity of phosphorus, can be increased by a factor of 4 through "*soft*" excitation, as demonstrated by the yellow 10 kV-spectrum shown in *Figure 6*.

Unfortunately, lowering the excitation voltage of the X-ray tube, which is favourable for the detection of phosphorus, is not effective for thickness measurement. The solution is to combine both types of excitation in one measurement (multiple-excitation). In the process, multiple spectra are obtained for one measurement.
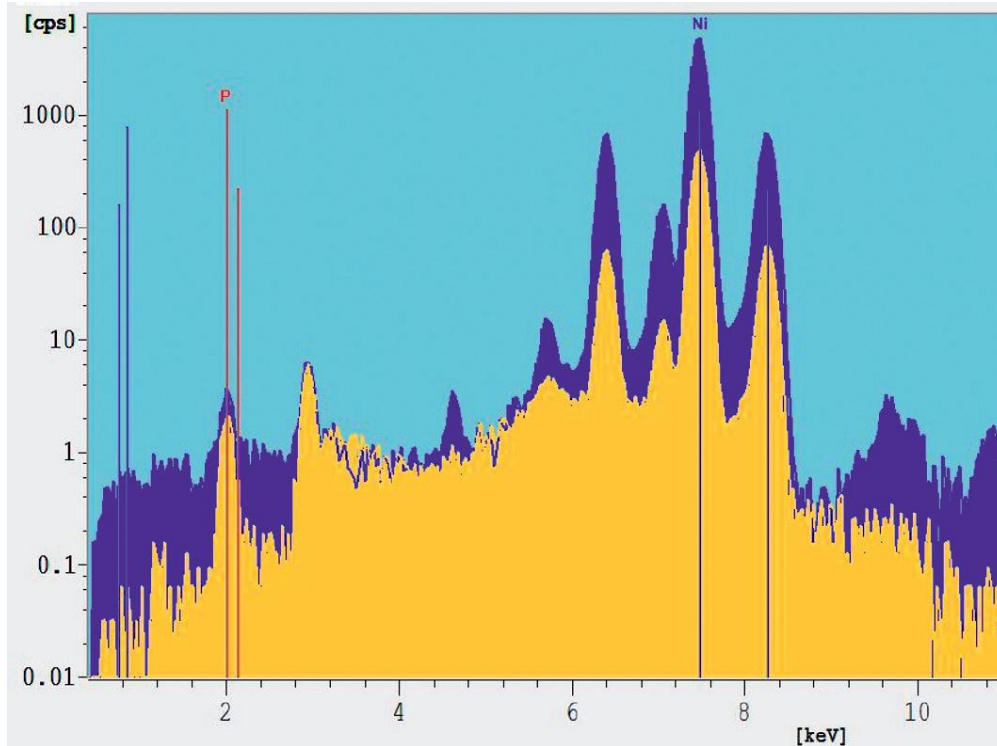

Figure 6: Fluorescence spectra (log intensity scale) of a NiP/Fe sample (14.3 μm, 9.3 % P) for different excitation conditions: 50 kV, 10 μm Ni-Filter (blue) and 10 kV non-filtered (yellow). Fischerscope® X-Ray XDV-SDD, aperture Ø 1 mm, anode current in both cases = 1 mA.

For EN measurement, two excitations are sufficient: the first 50 kV *"hard"* excitation is used for the coating thickness measurement and the "*soft*" 10 kV excitation for the phosphorus content.

3 Measurement Uncertainty and Reference Samples

Although standards-free measurements do deliver quite reasonable results with properly set-up instruments (as shown in *Table 1*), a calibration with reference samples and corresponding adjustment is essential for accurate routine measurement. For this reason, calibration standard sets consisting of several nickel/phosphorus samples with various phosphorus concentrations have been developed for the substrate materials iron, aluminium, copper and for printed circuit boards. Traceability is established using ICP-OES analyses of three independent laboratories. Their good correlation to standards-free XRF values is presented in *Figure 7*. Deviations from the regression line have various causes. As a whole, they represent the systematic measurement uncertainty, which can be estimated at about 0.3% phosphorus. Thus, the total measurement uncertainty can be assessed to be about 0.5% phosphorus.
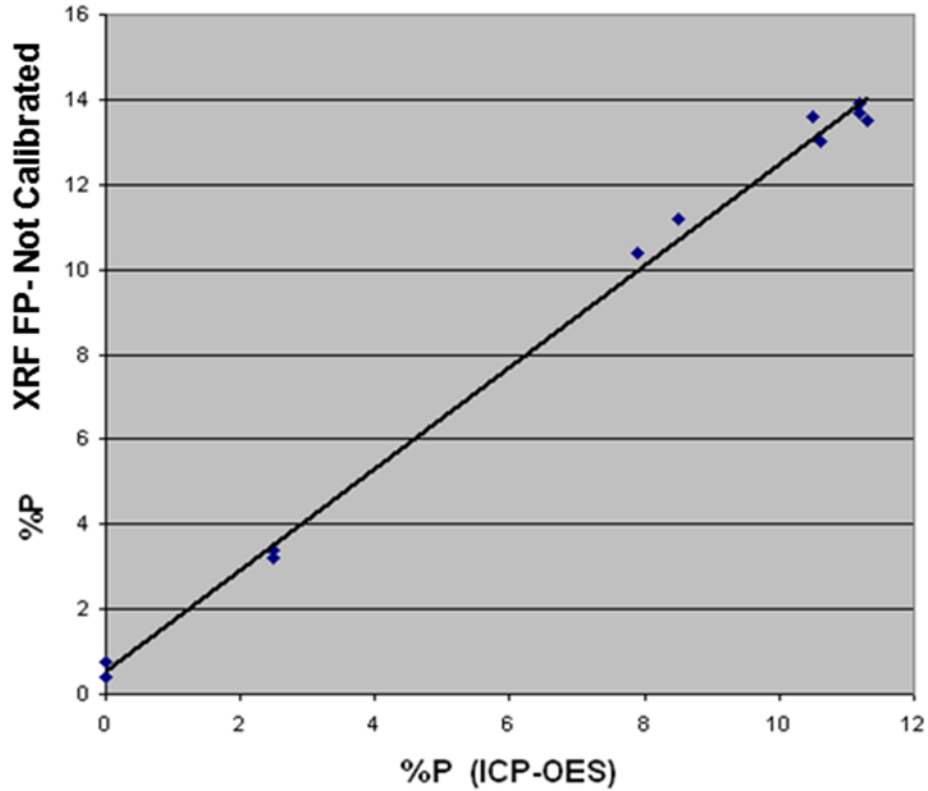
Figure 7: Comparison of the destructive chemical analysis (ICP-OES) with previously determined XRF results. XRF measurements were performed standards-free according to the method described in [2].

4 Measurement Examples

4.1 Nickel/Phosphorus on Aluminium – Thickness and Composition

Table 2 shows the measurement results from an application for determining the thickness and composition of a nickel/phosphorus coating on any desired substrate material.

Table 2: NiP/Al (hard disk): Excitation 50 kV with Al 0.5 mm filter and 10 kV non-filtered. Aperture Ø 3 mm, measuring time 20 s per excitation, 10 individual measurements at the same location (repeatability measurements)

Fischerscope® XRAY XDV-SDD		
Application: 290 / NiP/Al multiple times		
Single readings		
n= 1	P Ni1= 8.652 µm	P = 11.59 %
n= 2	P Ni1= 8.701 µm	P = 11.39 %
n= 3	P Ni1= 8.730 µm	P = 11.92 %
...		
n= 10	P Ni1= 8.733 µm	P = 11.79 %
Mean value	8.687 µm	11.57 %
Standard deviation	0.045 µm	0.232 %

4.3 Nickel-Phosphorus on a Printed Circuit Board

Printed circuit boards are an important application for nickel/phosphorus coatings, on top of which, additional gold and/or palladium coatings are applied. The phosphorus content cannot be determined through these surface layers – the low energy P-K emission is absorbed. So, Au and Pd must be stripped prior to analysis or the uncoated nickel/phosphorus coating must be measured. The measuring application must be designed such that the copper undercoat does not influence the spectra evaluation. Coatings of a few tenths of a micron can then be measured. The measurement uncertainty is comparable to the example in *Table 2*.

4.4 Phosphorus Only Analysis

The phosphorus content can be determined independent of the coating thickness if the thickness is greater than 3 μm (*Table 3*). Only the soft 10 kV excitation is used and the measuring time is half of that of the complete analysis.

Table 3: Measurement of the phosphorus concentration; XDV-SDD, 10 kV non-filtered, aperture Ø 3 mm, measuring time 30 s, 10 individual measurements at the same location (repeatability measurements)

Fischerscope® XRAY XDV-SDD	
Application: 325 / NiP	
Individual results	
n = 1	P = 11.43 %
n = 2	P = 11.36 %
n = 3	P = 11.68 %
	...
n = 10	P = 11.54 %
Mean value	11.72 % P
Standard deviation	0.219 % P
Measuring time	30 sec

5 Summary

New developments in XRF hardware and software technology have made it possible to simultaneously measure % phosphorous and NiP coating thickness in air. Being able to measure the phosphorous content directly now allows determination of the % phosphorous in electroless Ni-platings on substrates in addition to iron, such as, Al or even non metallic substrates. Instruments with SDDs can measure the P-K radiation quite well using soft primary excitation (10 kV, non-filtered). Coating thickness is determined using harder excitation (30 keV or 50 kV).

The information depth for phosphorus is relatively low (<1 μm) due to the low energy of P-K fluorescence.

Conventional indirect determination of phosphorus can still be regarded as a relatively robust method with proportional counter tube instruments – the only option with these instruments.

The use of appropriate reference standards is highly recommended.

Bibliography

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[3] V. Rößiger, G. Conrad, Metalloberfläche München 43 (1989) 12, 569