Technical Article

Analysis of Electroless Nickel Solutions By Anion Chromatography

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The principal appeal of ion chromatography (IC) as an analytical technique lies in the ability to rapidly analyze a mixture of ions of widely varying concentrations and properties in a single elution. It is therefore not surprising that IC has been considered as a potentially powerful technique for the complete analysis of all electroless nickel (EN) solution anions. However, the use of the technique has been hampered by the similar ion exchange selectivity coefficients of many of the EN solution anions, making it difficult to achieve effective separation of all the EN bath



anions on an ion chromatography column. This article addresses the separation issue and describes a method that has been developed for separating the organic acid anions commonly found in an electroless nickel bath from the inorganic anions. By using a high-capacity anion exchange column and carefully selecting a mixed isocratic-gradient elution with sodium hydroxide, the separation and quantification of all the component anions in a surrogate electroless nickel solution (hypophosphite, orthophosphite, sulfate, propanoic and succinic acid) were achieved. The analysis of trivalent anions such as citrate and orthophosphate was also shown to be possible.

The electroless nickel (EN) process has emerged as the most important industrial catalytic plating process for producing metal deposits with superior physical properties and for use in depositing metal coatings on small parts, or in situations in which electrodeposition is not possible.¹⁻³ All of the ions in an EN bath will, to varying extents, influence the deposit type and deposition rate, and in order to

Nuts & Bolts: What This Paper Means To You

One of the critical things in operating an electroless nickel bath is control of chemistry. Ion chromatography has shown great potential in providing a one-shot analysis of the whole bath, with a single snapshot that shows the "fingerprint" of the bath. The trouble is, many of those fingerprint lines overlap one another so you can't tell which is which. This work looks into that, with the intent of separating the wheat from the chaff, so you can use that "fingerprint" and eliminate many test tubes, beakers and a lot of analysis time. produce a high-quality EN coat, the concentration of the ions in the bath should be monitored and controlled.²

The nickel cation can be quantified by EDTA titration, but there is no simple method available for the analysis of the EN bath anions. When sodium hypophosphite is used as a reducing agent, the concentration of hypophosphite can be roughly estimated from its molar ratio with nickel (when the nickel concentration is known) but it is more commonly determined by iodine titration.⁴ The product of hypophosphite oxidation is orthophosphite, which can be quantified by a number of titration methods.^{5,6} The strengths and weaknesses of the various analytical methods for hypophosphite and orthophosphite determination have been the subject of two reviews.^{7,8}

The wet analytical methods are sufficiently accurate for most EN plating operations and are ideally suited to small jobshops requiring little capital investment. For larger plating shops with a number of EN baths and for EN plating solution suppliers, however, the wet methods are time-consuming and do not provide information on the concentration of the other bath anions, such as sulfate (from nickel sulfate) and the organic acid complexing agents.

Ion chromatography offers an opportunity to accurately quantify all EN bath anions in a single analysis. The use of ion chromatography in the plating industry and for the analysis of EN bath anions has been discussed in a number of publications.^{8,9} As far as the authors are aware, however, there have been no ion chromatograms presented that clearly show that IC can reliably separate and quantify all of the anions (including the organic acids) in an EN bath. The real challenge for ion chromatography in the analysis of electroless nickel baths work is in the separation of the organic acid anions from the inorganic anions. This article presents the results of the successful separation of organic acids commonly found in EN baths from the inorganic anions, hypophosphite, orthophosphite and sulfate. This

Table 1Concentration of Each ComponentIn a Simulated Spent Electroless Nickel Bath

Component	Concentration (g/L)	Concentration (Molar)
Nickel	5	0.086
Sodium	75	3.260
Orthophosphite	135	1.687
Sulfate	60	0.625
Hypophosphite	15	0.230
Propanoic acid	10	0.135
Succinic acid	10	0.085

work was part of a larger effort to extend EN bath life by electrodialysis using a surrogate EN solution. In order to assess the success of bath life extension, it was necessary to develop an ion chromatography procedure to monitor the fate of the anions.

Experimental Procedure Chemicals & Solutions

The composition of the surrogate spent electroless nickel bath, based on typical spent EN baths^{2,3,10} is shown in Table 1, along with the concentration of each component. The following chemicals were used in bath preparation: nickel sulfate hexahydrate (98+%), sodium phosphite pentahydrate (98%), phosphorus acid (98%), sodium sulfate (99+%), sodium hypophosphite monohydrate (99%), propanoic acid (99%) and succinic acid (99%). The pH of the surrogate electroless nickel solution was 4.5. The standards, samples and eluents were prepared in deionized ultrapure water (18 M Ω). The hydroxide eluents were prepared from 50 wt% NaOH and were degassed by sonication under vacuum for one hour before use, and then stored under compressed nitrogen gas.

Sample Preparation & Chromatographic Conditions

A 1/10,000 dilution with deionized water (two successive 1/100 serial dilutions) was carried out on the surrogate electroless nickel bath to bring the anions within the calibration range for IC analysis. A $10-\mu$ L aliquot of this sample was injected on the column without further preparation using an auto-injection carrousel.

The ion chromatography analyses were carried out on an ion chromatograph^a with a GP50 gradient pump and ED40

 ^a Dionex 500, Dionex Corp., Sunnyvale, CA
^b Dionex Peaknet, Dionex Corp., Sunnyvale, CA
^c ASRS[®], Dionex Corp., Sunnyvale, CA
^d IonPac[®] ASII-HC Column, Dionex Corp., Sunnyvale, CA electrochemical detector. A computer with special capability software^b was used to acquire the experimental data. The detector was operated in conductivity mode (sensitivity = 100 mA) using an anion self-regenerating suppressor^c to suppress high hydroxide concentrations, and permitted steep hydroxide gradients to be used without a substantial increase in background conductivity.

A high-capacity 4-mm analytical column^d (2 x 250 mm), preceded by a guard column (2 x 50 mm), was used for the anion separations. The anion exchange column provided rapid profiling of inorganic anions and organic acid anions, and was composed of ethylvinylbenzene crosslinked with 55% divinylbenzene functionalized with quaternary ammonium groups.

A gradient mixer and a 2 mm diameter anion trap column (ATC) were placed before the guard column.

The gradient mixer was required to mix the different incoming eluents, and the ATC was necessary to remove residual carbonate ions that may have been introduced to the eluent *via* contact with the atmosphere. The elution system used for anion separation was a mixed isocratic-gradient system derived from three eluent reservoirs: ultrapure water, 3 mM NaOH and 100 mM NaOH. The hydroxide gradient conditions for column conditioning and sample analysis are shown in Table 2.

Periodically, the exit from the ATC was bypassed to a beaker and 100% NaOH was passed through the ATC for one hour to flush out accumulated carbonate ions. The ATC was then rinsed with 30% NaOH before reattachment to the AG-11 guard column.

Results

Anion Separation Resolution & Interference

A typical ion chromatogram of a simulated spent EN bath is shown in Fig. 1. Table 3 shows the elution retention times of the anions in a surrogate electroless nickel solution under the chromatographic conditions described in Table 2. The anions are eluted in order of

Table 2Hydroxide Gradient Conditions for Column Conditioning & Calibration*

Time, min	Ultrapure	3mM naOH,	100mM NaOH,	Eluent flow
	water, %	%	%	rate, mL/min
		Conditioning		
0	70	0	30	1.53
0	70	0	30	1.5
31	0	100	0	1.5
150	0	100	0	1.5
		Sample run		
0.0	0	100	0	1.0
4.0	0	100	0	1.0
4.5	86	0	14	1.5
9.5	86	0	14	1.0
10.0	84	0	16	1.0
16.0	84	0	16	1.0
16.5	0	100	0	1.5
19.0	0	100	0	1.0

*Sample run on a chromatography column to separate the anions in a surrogate electroless nickel solution.

Table 3EN Bath Analysis by Ion Chromatography

Anion	Retention time, min	Calibration range, ppm	QCS, ppm	Linearity, R ²	% Recovery	% RSD
Hypophosphite	5.2	0.1 - 20	3.0	0.9999	97.8	1.9
Propanate	5.8	0.1 - 20	3.0	0.9986	103.5	0.5
Orthophosphite	12.6	0.5 - 100	30	0.9999	99.1	0.1
Succinate	13.2	0.1 - 20	3.0	0.9996	97.4	1.1
Sulfate	17.2	0.5 - 100	15	0.9994	95.4	0.5
QCS: Quality Control	Standard	RSD: Relative Stand	lard Deviations			

their valence, with monovalent hypophosphite and propanate eluting first, then divalent orthophosphite, succinate and sulfate eluting later. Both hypophosphite and propanate and then orthophosphite and succinate elute close together (within 0.5 min of each other). The eluent composition, *i.e.*, hydroxide concentration, must be carefully adjusted and regulated to obtain the optimum separation of hypophosphite from propanate and orthophosphite from succinate. Deviations from this eluent composition either lead to tailing (hydroxide concentration too low) or peak overlapping (hydroxide concentration too high). If the column is always pre-conditioned in the same manner before a calibration or sample run, there is little shift in retention times.

The presence of nickel in diluted solutions from electroless nickel bath samples does not appear to interfere with the chromatography analysis. The accompanying nickel is likely to form insoluble $Ni(OH)_2$ when mixed with the eluent, which may precipitate on the column. However, over a period of 12 months, there was no evidence that the possible precipitation of $Ni(OH)_2$ impaired column performance or interfered with the analysis. If the precipitation of $Ni(OH)_2$ does appear to be a problem, the addition of a strong nickel complexing agent such as EDTA to the sample solution should prevent precipitate formation at the pH encountered in the eluent.

Calibration & Linearity

The five calibration standards were prepared in deionized water from a composite stock solution that contained all the surrogate electroless nickel solution components. The calibration standard concentration range (shown in Table 3) was chosen to reflect the relative proportions of the components in a spent electroless nickel solution (*i.e.*, high concentrations of orthophosphite and sulfate and lower concentrations of hypophosphite and the organic acids). A calibration curve that includes the (0,0) point is constructed with previously mentioned software based on the integration of component peak area. The correlation coefficients for the concentrationpeak area calibration curves of all the EN solution components are greater than 0.998 (Table 3).

Accuracy, Precision & Detection Limits

A quality control standard (QCS) was prepared in deionized water from a similar but separate stock solution to that used for preparing the calibration standards. The QCS was used for assessing the accuracy and precision of the chromatography method. The concentration of the QCS for each anion is given in Table 3. The percent recovery of the five anions in the QCS ranged from 95-105% demonstrating a method accuracy of \pm 5%. A percent relative standard deviation (RSD) calculation on five replicate injections of a QCS shows that the RSDs of the five components were all less than 2%. A practical quantitation limit (the concentration above which the results are considered valid due to decreased variability) of 1 ppm is desired for the IC method. In the case that a dilution of an electroless nickel solution results in one of the components being less than 1 ppm, a second lower dilution should be carried out to ensure that all anion concentrations are greater than 1 ppm. Five replicate injections of a second QCS containing 1 ppm of each component show recoveries of 90-110% and relative standards deviations of less than 10% for all components at this concentration.

Other Anions

Although the surrogate electroless nickel solution used in this work did not contain either trivalent orthophosphate or citrate, these anions are common in electroless nickel baths. The citrate may be present as a strong complexing agent, and orthophosphate can accumulate in aging electroless nickel baths due to orthophosphite oxidation. It is possible to elute (and probably quantify) both of these anions by increasing the hydroxide concentration in the eluent after sulfate elution (at 16 min in Table 2) to a 35:65 ratio of 100 mM NaOH:water. At this eluent composition, orthophosphate will elute first, followed by citrate and the chromatography run time will increase up to 25-28 min.

Electroless nickel baths may also contain combinations of other monovalent and divalent organic acids. Divalent malic acid is frequently present in EN solutions; this acid anion can be separated from divalent orthophosphite under the chromatographic conditions employed in this work. However, the presence of a number of divalent organic acids may represent a separation problem. In addition, certain monovalent acids were found to be very difficult to resolve from hypophosphite, e.g., acetic acid. It was thought that this resolution problem could be overcome by using a mixed organic-aqueous eluent system, thereby exploiting the lower polarity of the acetate anion and modifying its ion-exchange selectivity. The hydroxide-based eluent was mixed in varying proportions with different organic solvents-such as acetonitrile, methanol and tetrahydrofuran-and 1:1 mixtures of acetate:hypophosphite were injected into the IC column using these eluents. However, these mixed organic-aqueous eluents did not provide significant resolution of the overlapping hypophosphite/acetate peaks.

Conclusions

This research provides an ion chromatography method for the separation and quantification of organic acid and inorganic anions commonly found in electroless nickel solutions. Of course, the anionic composition of proprietary electroless solutions will vary according to supplier and the plating application. We therefore recommend that careful attention be paid to determine if it is possible to separate all the EN solution anions by ion chromatography in a given situation. It may be that ion chromatography can only be used to analyze certain EN bath solutions depending on the anionic composition. We hope, however, that this research may encourage EN plating shops and suppliers to consider and further explore the incorporation of ion chromatography into their analytical "toolbox" for the routine testing of electroless nickel solutions.

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