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# Determination of inorganic and organic ions in nickel-plating baths by capillary electrophoresis

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## Abstract

Analysis of nickel-plating baths for various anions, organic acids and cations was performed by capillary electrophoresis. Analysis of these ions is important in relation to the effectiveness of the plating bath. Analysis of anions and organic acids in these plating baths was accomplished by direct UV detection at 185 nm and a phosphate electrolyte. Nickel and other cations were determined by indirect UV detection at 185 nm as well. Total analysis times of less than 7 min for anion and organic acid analysis and 5.5 min for nickel and other cations analysis could be achieved using these electrolytes. Changeover time from anion to cation analysis by capillary ion electrophoresis was accomplished in less than 10 min.

*Keywords:* Organic acids; Inorganic cations

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## 1. Introduction

Electroless plating baths are used extensively for the plating of various metals onto surfaces for both industrial and commercial products. Electroless plating is a technique in which no external voltage is used. Instead, it is a chemical means of plating involving the chemical reduction and oxidation for the plating of the particular metal onto the desired surface. Electroless nickel plating is one of the most used plating operations done and the technique has been described elsewhere [1]. The analysis of these plating baths is important in determining the quality and effectiveness of the plating operation. Organic acids such as acetate and citrate are added to electroless nickel plating baths as complexing agents. There are several reasons for adding complexing agents to the bath, some of which include buffering, and the prevention of nickel salt precipitation. Furthermore, the levels of organic acids present affect the deposition reaction [1]. For these reasons monitoring of the organic acids as well as other anions is

important [1–3]. The current methods for monitoring of these organic acids is by ion chromatography (IC) employing a gradient separation which can be very time consuming.

Analysis of these inorganic and organic ions was done using a capillary electrophoretic technique which has been developed for the rapid analysis of low-molecular-weight inorganic and organic ions [4]. This technique has been shown to provide comparable results to conventional IC as well as offer the advantage of speed, ease of use and fast changeover from one analysis to another [5–8]. For anion analysis an osmotic flow modifier, OFM, is added to the electrolyte as an additive that reverses the normally cathodic direction of the electroosmotic flow (EOF) found in fused-silica capillaries. This creates a co-electroosmotic condition that augments the mobility of the analytes. Cation analysis using a UV Cat-1 and hydroxyisobutyric acid (HIBA) electrolyte has been shown as well to be a sensitive technique for cation analysis [9]. No OFM is required for cation analysis since the natural EOF is in

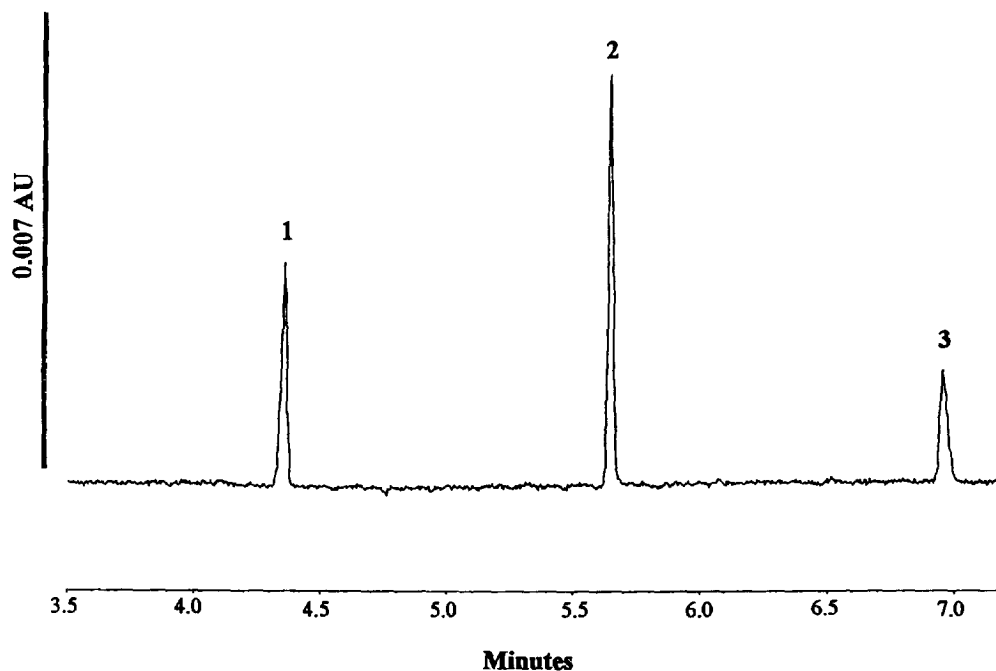


Fig. 1. Electropherogram of anion standard. CE conditions: fused-silica 60 cm $\times$ 75  $\mu$ m I.D. capillary; voltage, 18 kV (negative); electrolyte, 25 mM Phosphate–0.5 mM OFM-OH; direct UV detection at 185 nm; hydrostatic injection (10 cm for 30 s). Solutes: 1, chloride (3.0 mg/l); 2, citric acid (8.0 mg/l); 3, acetic acid (3.0 mg/l).

the same direction as the cation migration and thus augments the separation. In this paper several electrodeless nickel plating baths were analyzed prior to and during the plating operation.

## 2. Experimental

### 2.1. Instrumentation

The capillary electrophoresis (CE) system employed was the Quanta<sup>TM</sup> 4000E CIA (Waters Chromatography Division of Millipore, Milford, MA, USA). A Hg lamp was used for direct UV detection at 185 nm for anion analysis and indirect UV detection at 185 nm for cation analysis. AccuSep<sup>TM</sup> polyimide fused-silica capillaries of dimension 75  $\mu$ m I.D. $\times$ 60 cm were used throughout. Data acquisition was carried out with a Waters Millennium<sup>TM</sup> 2010 Chromatography Manager with a SAT/IN module, for signal collection, connected to the CE

and data station with the signal polarity inverted from the CE.

### 2.2. Preparation of electrolytes

High purity water (Milli-Q<sup>TM</sup>) was used to prepare all solutions (Millipore). The working electrolyte for anion analysis was a solution of 25 mM phosphate and 0.5 mM OFM in the hydroxide form. The phosphate electrolyte was prepared from a packet (Waters) containing a preweighed amount of mono and di-basic phosphate such that diluting the contents to 200 ml gave a 25 mM solution with a natural pH of approximately 7.0. Osmotic flow modifier (OFM) was obtained in the Br form as a 20 mM concentrate from Waters. Anion-exchange cartridges (IC-OH cartridges, Alltech Associates, Deerfield, IL, USA) were used to convert the OFM to the hydroxide form by simply passing the OFM through the cartridge.

For cation analysis UV Cat-1 and HIBA were obtained from Waters. The working electrolyte for cation analysis was a solution of 4.0 mM UV Cat-1

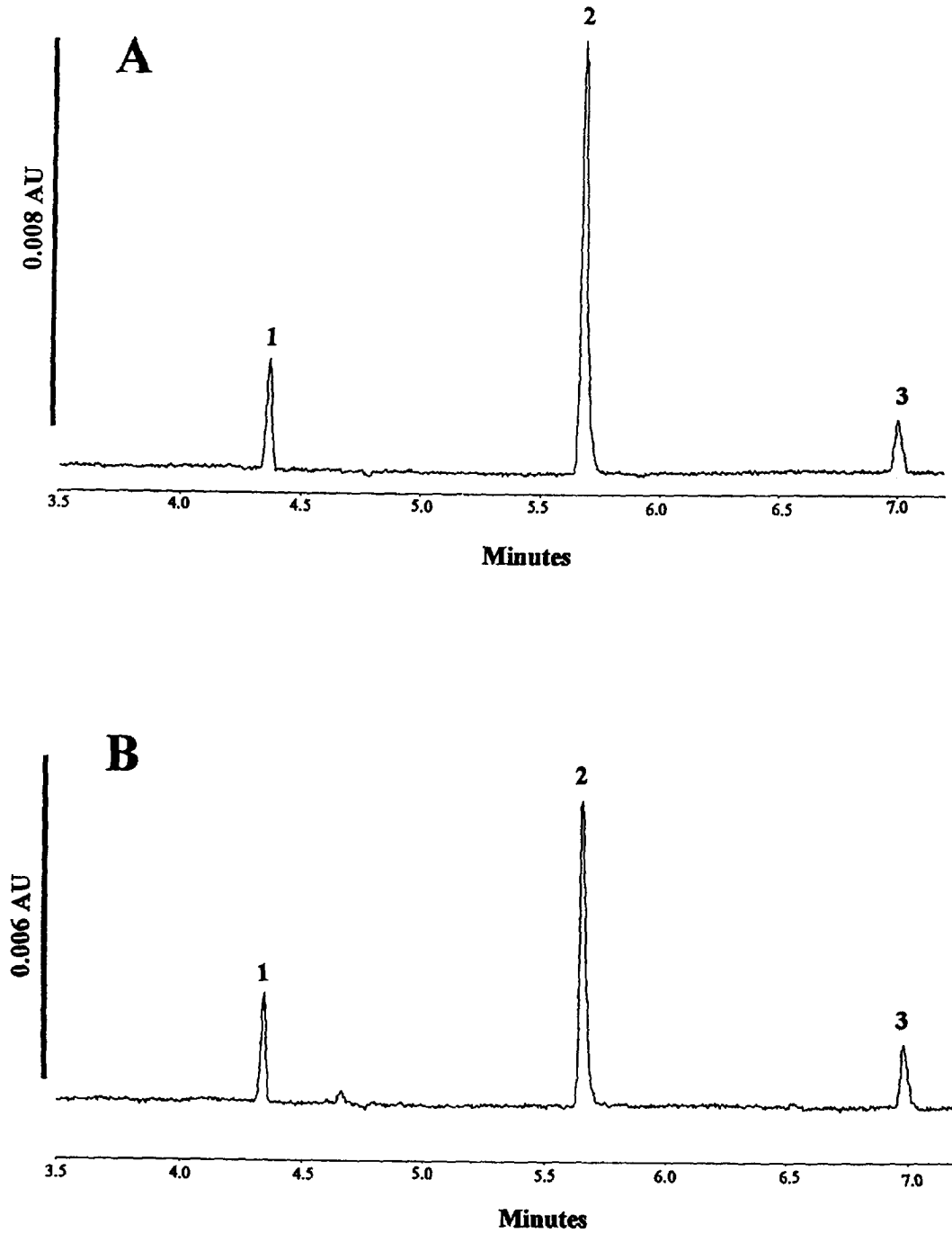


Fig. 2. Electropherogram of plating sample before (a) and after plating (b). Diluted 0.02–100 ml. Conditions as stated in Fig. 1. Solutes: (A) 1, chloride (8457 mg/l); 2, citric acid (73 017 mg/l); 3, acetic acid (9171 mg/l); (B) 1, chloride (7312 mg/l); 2, citric acid (47 434 mg/l); 3, acetic acid (9366 mg/l).

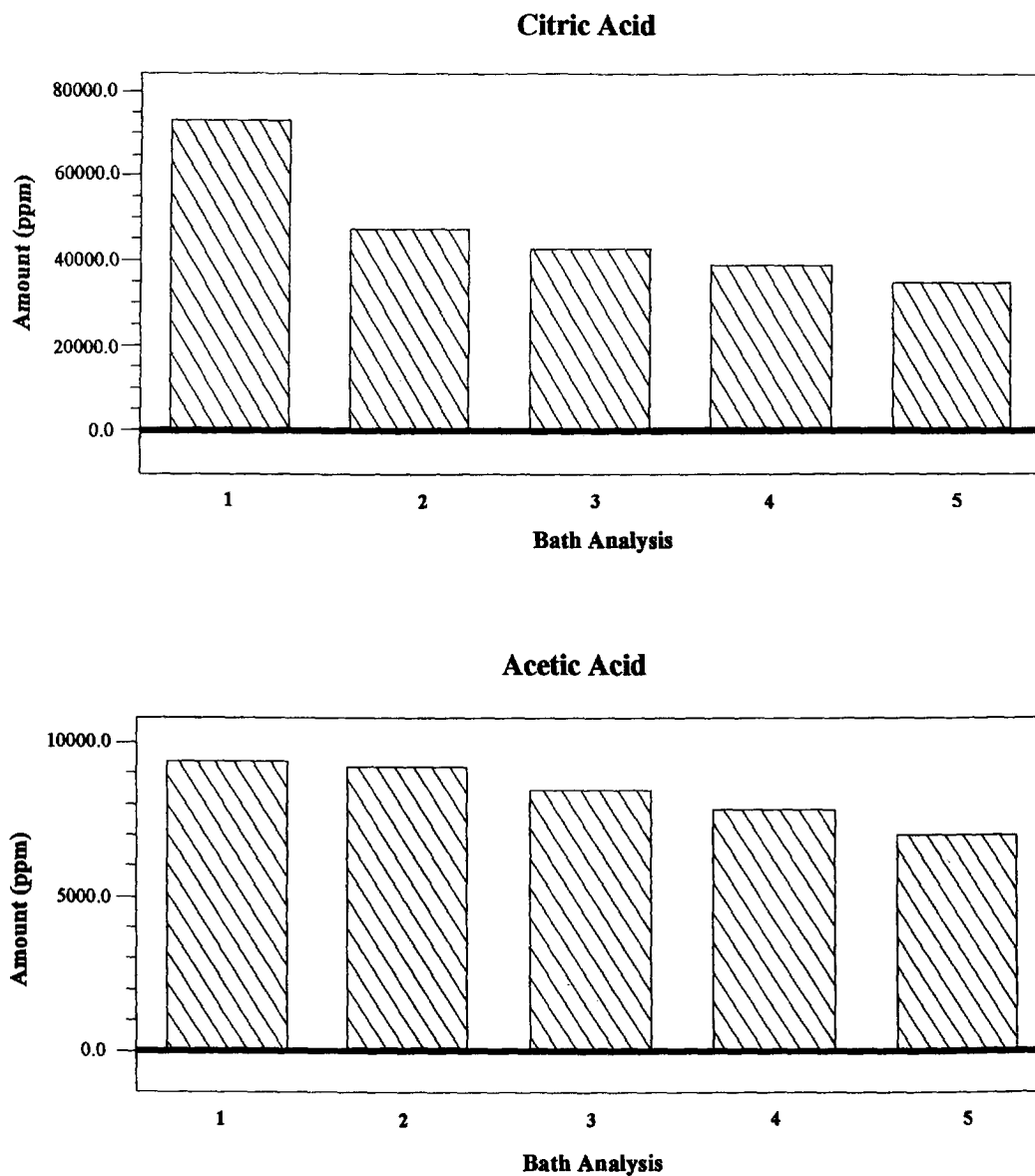


Fig. 3. Control chart for citric and acetic acids monitored over several hours. Numbers represent new (unused) bath (1) and progressive samples during the plating operation (2–5).

and 6.5 mM HIBA with a natural pH of approximately 4.4. All working electrolytes were prepared fresh daily and degassed prior to use.

### 2.3. Sample information

Samples of various electroless nickel plating baths prior to (new) and during the plating operation (used) were analyzed by capillary electrophoresis (CE).

Samples were diluted in high purity water and filtered prior to analysis.

### 2.4. Standard information

Standards were prepared as concentrates from their salts and diluted to appropriate amounts in high purity water. All standards used were of ACS grade or better. Calibration curves were calculated from

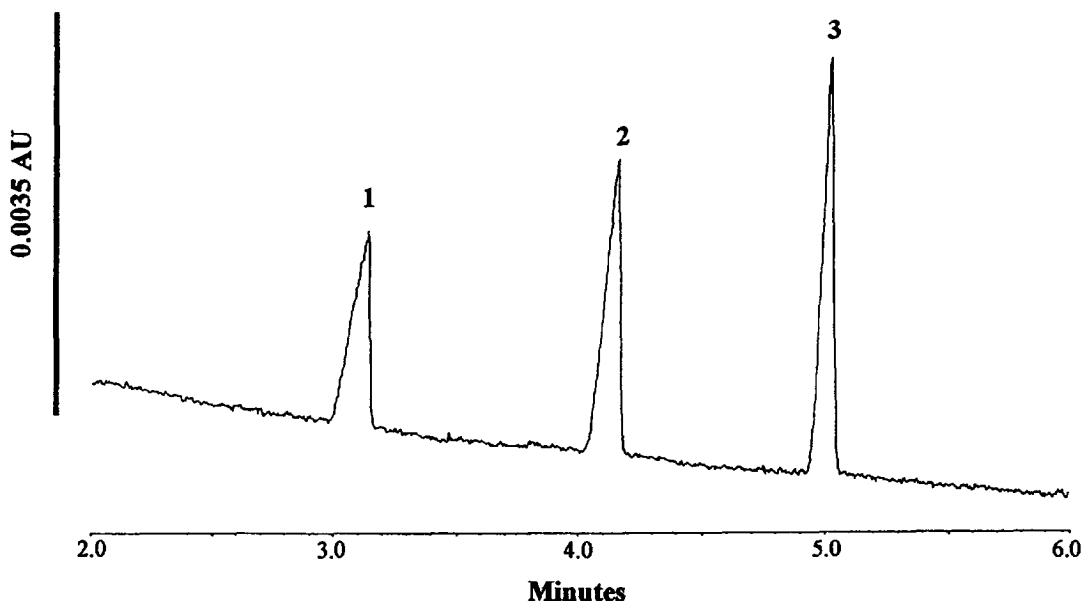


Fig. 4. Electropherogram of cation standard. CE conditions: fused-silica 60 cm $\times$ 75  $\mu$ m I.D. capillary; voltage, 20 kV (positive); electrolyte, 4.0 mM UV Cat-1–6.5 mM HIBA; indirect UV detection at 185 nm; hydrostatic injection (10 cm for 30 s). Solutes: 1, ammonium (4.0 mg/l); 2, sodium (4 mg/l); 3, nickel (6.0 mg/l).

duplicate injections of three different levels of standards with a straight line forced through zero drawn. Correlation coefficients ( $r^2$ ) of 0.99 $x$  with  $x \geq 7$  were achieved.

### 3. Results and discussion

Fig. 1 is an electropherogram of a standard containing the anions and organic acids expected to be in the bath. Fig. 2 is an electropherogram of a plating bath solution prior to being used (Fig. 2A) and after being used for plating operations (Fig. 2B). As can be seen the levels of citric and acetic acid drop which is expected since they are the main complexing agents. Using the phosphate electrolyte and CE control software, monitoring of a nickel plating bath was done over several hours and a control chart generated (Fig. 3) for the baths. This chart demonstrates the ability to monitor the organic acid levels of the citric and acetic acids over a period of time. The value of this information is in determining how the quality of plating is affected by the loss of each organic acid. Based on this preliminary data, citric acid is depleted at a higher rate compared to

acetic. Very little is known as to what effect the loss of these organic acids or anions has on the plating process. Further work will investigate how this effects the quality of the plating.

Analysis of cations and free nickel in the bath was also performed. Changeover from anions to cations by CE was achieved in less than 10 min. Since the separation uses a hollow fused-silica capillary, little equilibration of the capillary or system is required. Fig. 4 is an electropherogram of a cation standard containing ammonium, sodium and nickel. Fig. 5 is an electropherogram of the plating bath prior to (Fig. 5A) and after being used (Fig. 5B). As can be seen a reduction in nickel and ammonium is found, as well as the formation of several unknown peaks near sodium. These peaks may be small amine compounds which could have been introduced into the bath from the cleaning process of the parts used for plating, or as contaminants in the bath reservoir.

### 4. Conclusion

Overall, CE permitted the rapid analysis of anions and cations in electroless nickel plating baths. Analy-

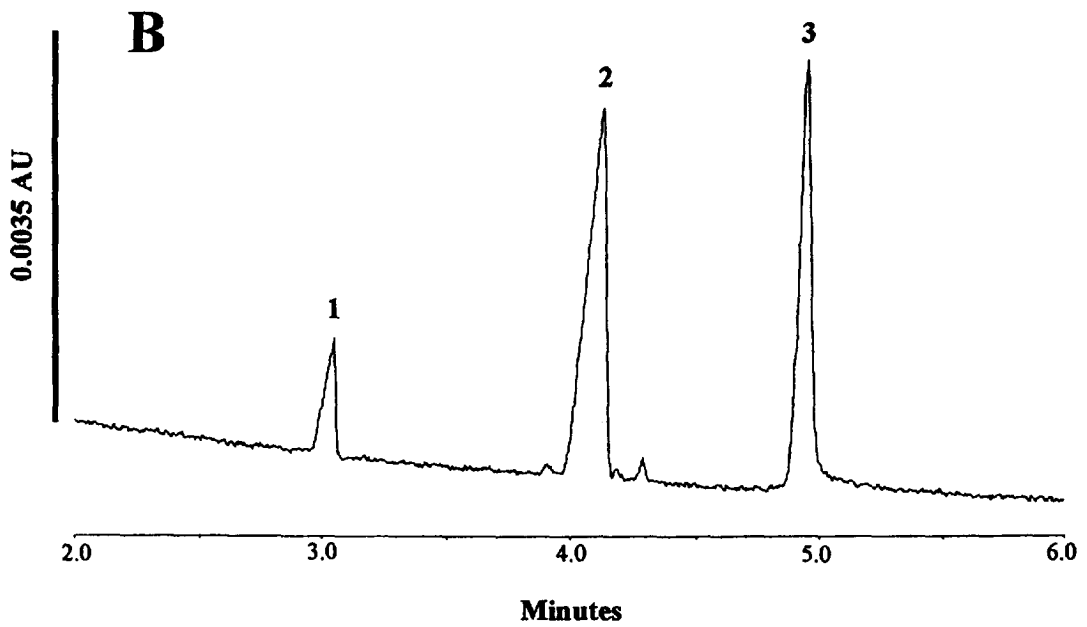
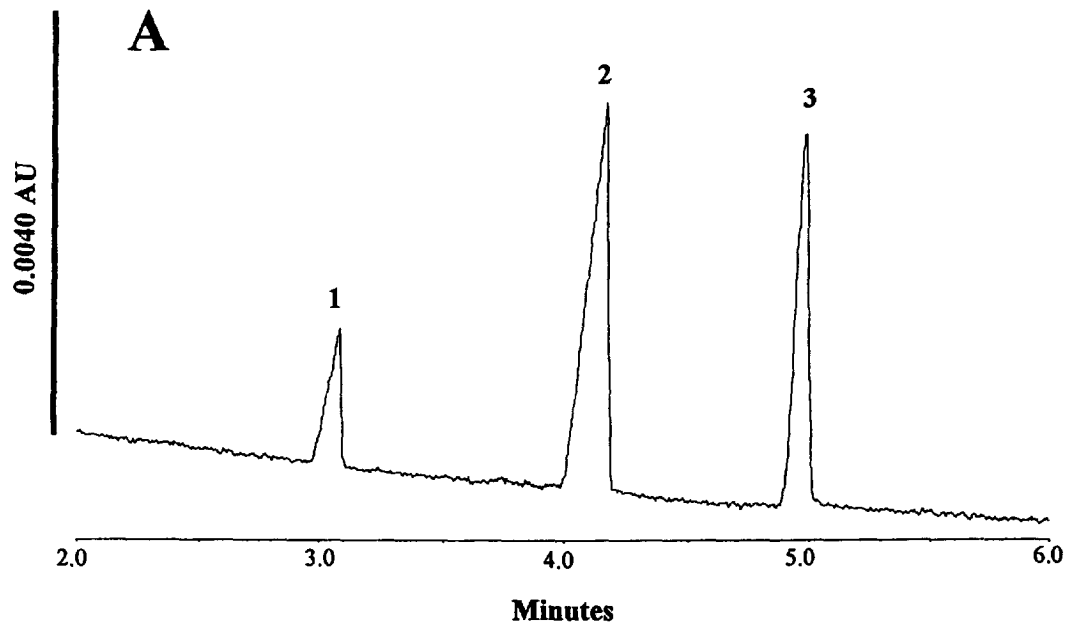


Fig. 5. Electropherogram of plating solutions new (A) and after being used (B). Samples were diluted 0.025–100 ml. Conditions as stated in Fig. 4. Solutes: (a) 1, ammonium (12 008.0 mg/l); 2, sodium (34 760.0 mg/l); 3, nickel (29 785.0 mg/l); (b) 1, ammonium (6594.0 mg/l); 2, sodium (30 000.0 mg/l); 3, nickel (27 773.0 mg/l).

sis times of less than 5.0 min for anions and organic acids was possible using a chromate electrolyte and under 7.5 min using a phosphate electrolyte. Cation analysis was possible in less than 5 min with a changeover time of less than 10 min from anion to cation analysis

## References

- [1] G.O. Mallory and J.B. Hajdu, *Electroless Plating*, AESF Press, Orlando, FL, 1990.
- [2] P. Jandik, W.R. Jones, B.J. Wildman, J. Krol and A.L. Heckenberg, *Methods for Monitoring Plating Baths used in Manufacturing of PC Boards*, Presented at the AESF conference, 1989.
- [3] P. Jandik, A.L. Heckenberg and R.L. Lacione, *Applications of UV detection to the Analysis of Organic Additives in Plating Solutions*, AESF Analytical Methods Symposium, 1988.
- [4] P. Jandik, W.R. Jones, A. Weston and P.R. Brown, *LC·GC*, 9 (1991) 634.
- [5] S.A. Oehrle, *J. Chromatogr. A*, 671 (1994) 383.
- [6] J.P. Romano and J. Krol, *J. Chromatogr.*, 640 (1993) 403.
- [7] J.P. Romano, J. Krol, G.F. Fallick, S.A. Oehrle and M. Benvenuti, *Capillary Ion Electrophoresis; An Effective Technique for Analyzing Inorganic and Small Organic Ions in Environmental Matrices*, Presented at the EnviroACS conference, 1995.
- [8] S.A. Oehrle, *J. Chromatogr.*, (1996) CHROMSYMP 3397.
- [9] A. Weston, P.R. Brown, P.R. Jandik, W.R. Jones and A.L. Heckenberg, *J. Chromatogr.*, 593 (1992) 289.