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Analysis of Inorganic and Organic Anions in Galvanic Samples Using the Agilent 7100 CE

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Abstract

This application note presents the determination of inorganic and organic anions in galvanic samples using an Agilent 7100 CE and commercially available materials.

Introduction

Capillary electrophoresis (CE) has been demonstrated to be applicable for the monitoring of anions in galvanic samples.[1,2] The challenge in analyzing this type of sample is the aggressive sample matrix, with very high metal concentrations. CE has a major advantage over ion chromatography (IC) in this respect, because of the increased robustness of free capillary columns compared to the packed columns used in IC. CE also requires minimal sample preparation.[1]

Due to their inability to absorb UV light, the anions of interest must be analyzed using indirect detection in CE. An organic acid buffer[1] or plating bath buffer[2] can be used to enable indirect UV detection. The advantage of these ready-to-use buffers is that an electroosmotic flow (EOF) modifier is already included, which causes an EOF reversal, enabling rapid analysis of the anions.

In this application note, various galvanic samples were investigated using a ready-to-use plating bath buffer. The method was also applied to examine wastewater samples from galvanic baths.

Experimental

Tables 1 and 2 summarize the chemicals, consumables, and method parameters used in this application.

The experimental conditions of the acquisition method are summarized in Table 3.

The plating bath buffer was filled into three autosampler vials (polypropylene vials, 1 mL) by pipetting 350 μL into each vial. Two of these vials were used as "Inlet Home" and "Outlet Home" vials, and the third vial was only used for the preconditioning step. These vials can be used for six runs without refilling the buffer.

Table 1. Chemicals.

Position	Material	Supplier	Order Number
1	Sodium dihydrogen phosphate dihydrate	Merck	1.06342
2	Sodium phosphite dibasic pentahydrate	Sigma-Aldrich	04283
3	Sodium hypophosphite monohydrate	Sigma-Aldrich	S5012
4	Sodium chloride	Merck	1.06404
5	Sodium nitrate	Merck	1.06537
6	Sodium sulfate	Merck	1.06649
7	L-(−)-malic acid	Merck	8.00384
8	Lactic acid	Sigma-Aldrich	252476
9	Water (LC/MS grade)	Merck	1.15333

Table 2. Consumables.

Position	Material	Supplier	Part Number
1	Capillary: fs, 50 μm, 72 cm	Agilent	G1600-62211
2	Plating bath buffer	Agilent	5064-8236
3	Polypropylene vials, 1 mL	Agilent	5182-0567
4	Alignment interface, green	Agilent	G7100-60210
5	Snap caps, polyurethane	Agilent	5181-1512

Table 3. Instrument parameters.

Parameter	Value
Device	Agilent 7100 Capillary Electrophoresis System
Firmware	B.07.021
Electrolyte	Plating bath buffer
Capillary	Fused silica (fs), 50 μm id, 72 cm
Injection	30 s, 50 mbar, followed by 5 s, 50 mbar electrolyte solution
Detection	Indirect UV, signal: 350, 80 and reference: 245, 30
Voltage	−30 kV, ramp: 0.3 min
Temperature	20 °C
Preconditioning	1 bar, 180 s flush of the electrolyte solution

Preparation of the standard solutions

For the preparation of the stock solutions, the single salts were weighed and dissolved using purified water, so that a final concentration of 1,000 mg/L of each anion was obtained. Using these stock solutions, any mix standard solution can be prepared as required for the respective analysis of interest.

Results and discussion

Applying the conditions summarized in the Experimental section, a typical standard solution profile, applicable for galvanic bath analysis, can be obtained (Figure 1).

Figure 1 shows that a negative nickel peak can be detected simultaneously with the anions. This peak can be explained by the fact that, when using the plating bath buffer, the co-ion of the electrolyte acts as a complexing agent, and forms a negatively charged nickel complex . This complex has a higher UV absorption than the co-ion itself, which results in a negative peak. In principle, this negative peak could also be used to analyze the nickel content simultaneously with the anions. However, the calibration of the negative nickel peak is not linear here, due to the complex formation. Nevertheless, there are other CE methods that can be used to investigate the metal ions in electroplating baths.[1]
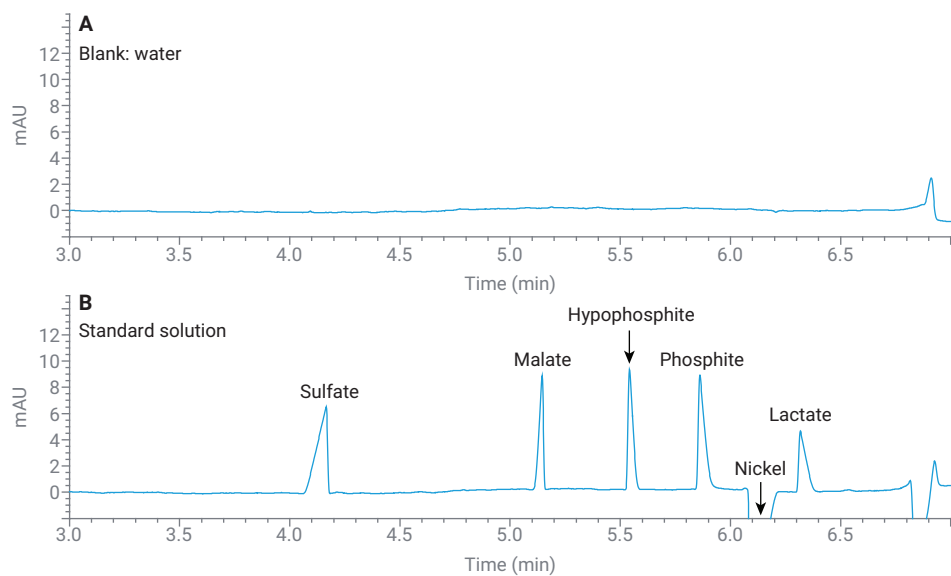

Figure 1. Blank and mixed standard solution, each 20 mg/L.

To verify quantification of the main anionic components, linearity was tested using a five-point calibration from 10 to 100 mg/L for six standard anions. The electropherograms obtained are shown in Figure 2.
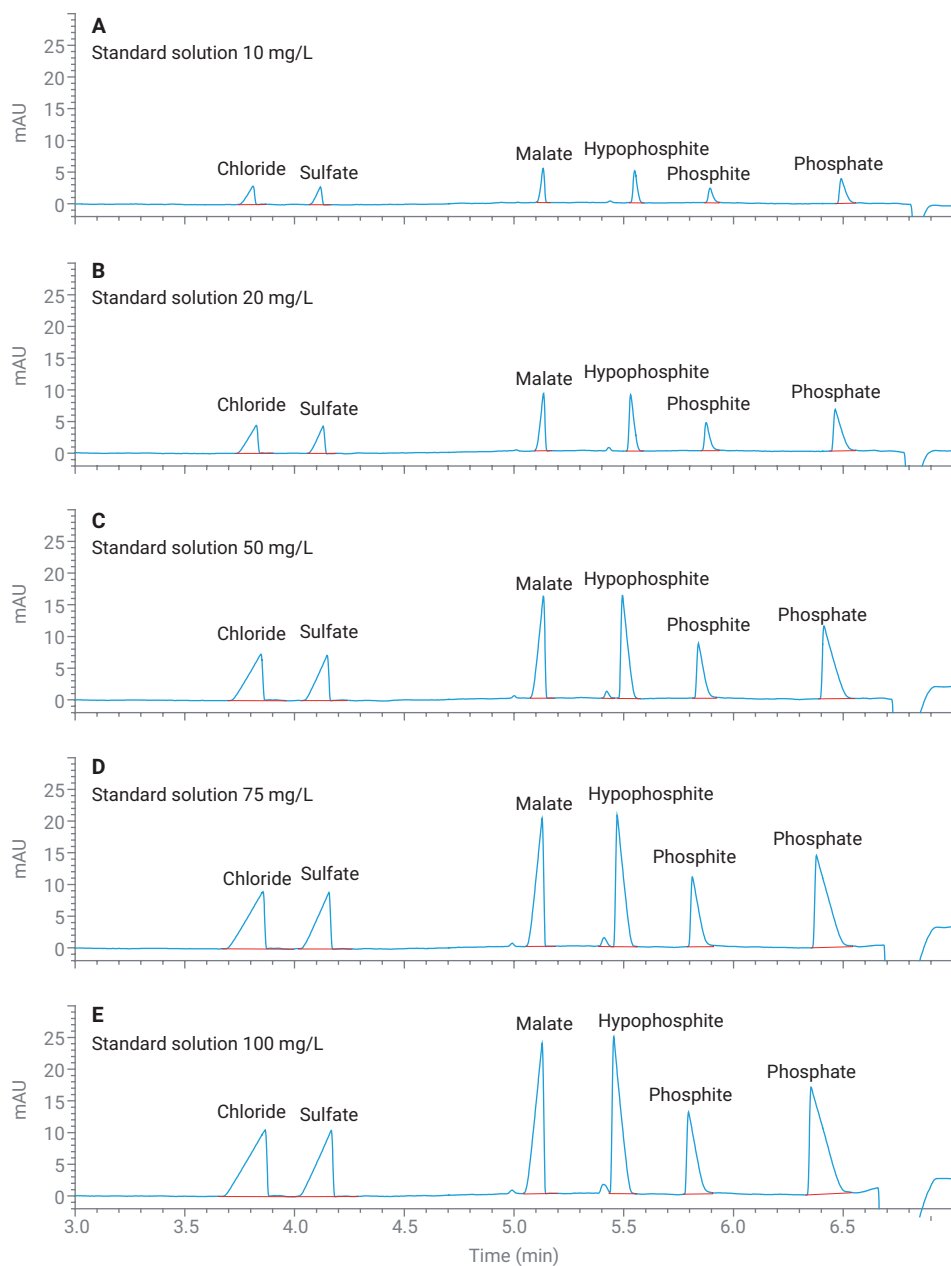

Figure 2. Standard solutions for calibration (10 to 100 mg/L).

Because of the excellent separation of all components, an automatic integration can be performed to determine the peak areas. The calibration results of four selected anions are summarized in Figure 3.

For each anion, a correlation of >0.999 was achieved. This result ensures that an accurate quantification can be performed. Due to this good correlation, it should be sufficient for routine analysis if only two points are calibrated or only one external standard is used.

With these method parameters, electroless nickel baths were investigated. Due to the deposition without external current, these kinds of baths can be used to coat electrically non-conductive components (e.g., those made of plastics such as polyamide or of ceramics). In addition to the nickel metal cations to be deposited, a reducing agent such as hypophosphite is required for chemical deposition.

Figure 4A shows an electropherogram obtained from an electroless nickel bath. The content of hypophosphite is drastically reduced, so phosphite can be seen as a large peak.

In recent years, the environmental aspects of electroplating processes have become an increasing focus of attention. As a result, more research is currently being carried out on methods for decomposing the resulting wastewater, such as special cleansing or UV radiation methods. Figure 4B shows an analysis of untreated wastewater. The water in Figure 4C has undergone a purification procedure, and the decomposition of hypophosphite and phosphite to phosphate is clearly visible.
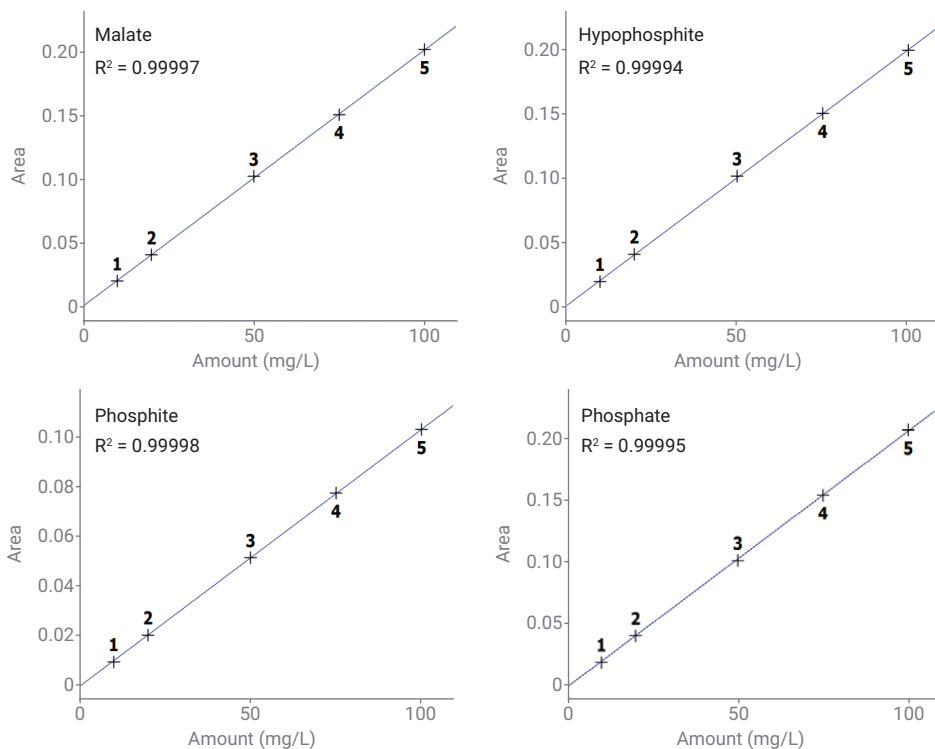
Figure 3. Calibration results of malate, hypophosphite, phosphite, and phosphate as an example. Calculated using Agilent ChemStation software.
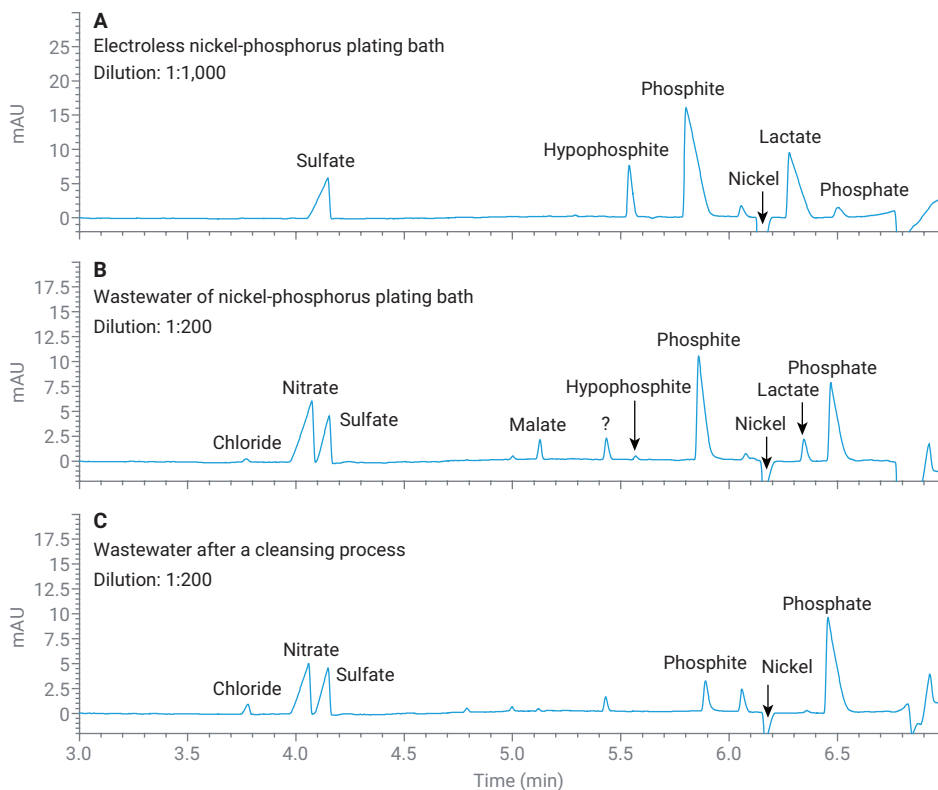
Figure 4. Samples of a nickel-phosphorus plating bath.

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Figure 5 shows three other baths used for electrodeposition. The baths were analyzed using the same CE method as the bath referred to in Figure 4.

These results demonstrate that the analysis of nickel-palladium, palladium-nickel, and zinc-nickel baths can be performed using CE.

Conclusion

The method presented in this application note can be used to analyze anionic analytes such as inorganic anions and organic acids in various galvanic baths for non-electrical (chemical) and electrical deposition of metals. The analytes of interest are well separated, allowing automatic integration of peak areas. The total separation time is 8 minutes. A further advantage is that the only sample preparation step needed is dilution. The procedure was carried out using currently available chemicals and materials.

Quantification was tested by a five-point calibration and correlations of >0.999 were obtained. The applicability of the method was demonstrated by sample measurement of different baths as well as of wastewater samples from baths.

References

1. Soga, T. Capillary Zone Electrophoresis for Electroless Plating Bath Samples. *Agilent Technologies application note*, publication number 5991-1105EN, **2012**.

2. Ion Analysis with Agilent Capillary Electrophoresis Systems. *Agilent Technologies application compendium*, publication number 5990-5244EN, **2010**, pp. 25–26.
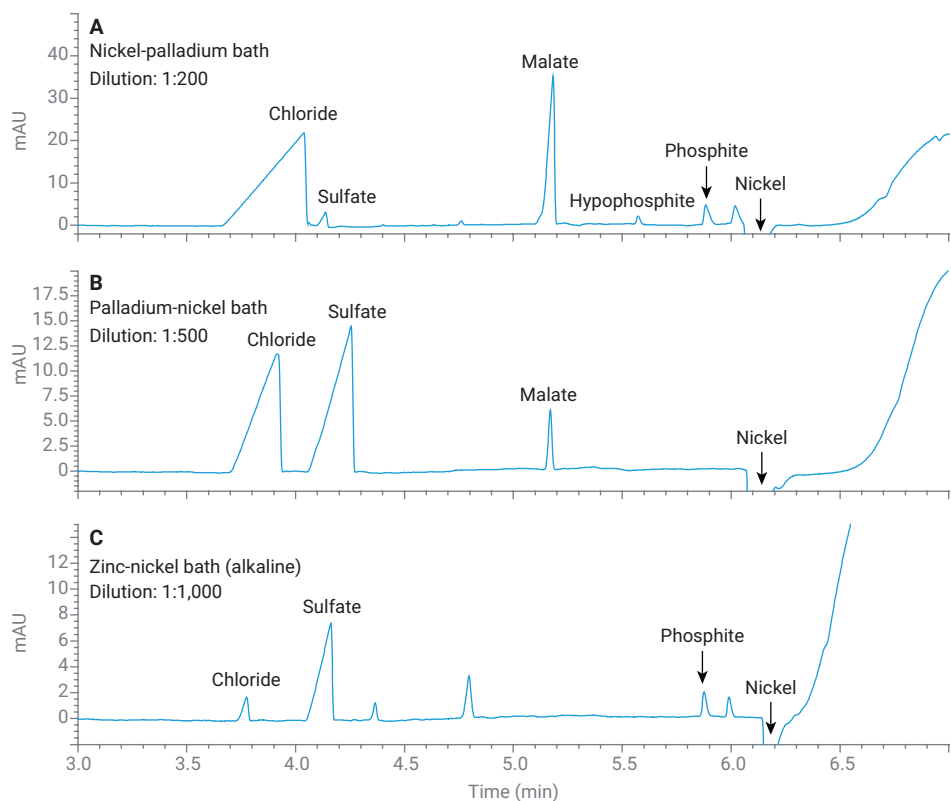
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Figure 5. Various baths for electrodeposition.

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