

# Determination of low-molecular-mass ionic compounds in electrodeposition coatings by capillary electrophoresis with conductivity detection

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## Abstract

A method for rapid and quantitative determination of small anionic compounds in electrodeposition coating samples has been developed. The separation was performed using capillary electrophoresis combined with nonsuppressed end-column conductivity detection. A series of Good's buffers covering a pH range from 6 to 10 was investigated to establish the most suitable separation system for this specific analytical problem. The results obtained with the method presented in this paper showed excellent agreement with those achieved by ion chromatography. © 1998 Elsevier Science B.V.

*Keywords:* Inorganic anions; Organic acids; Conductivity detection

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## 1. Introduction

The coating of workpieces e.g. car bodies by means of an electrodeposition process is an important methodology especially in the automotive or related industries. It is usually performed by introducing the object into a basin filled with a water-based electro-dipcoat [1], applying a voltage of 200–400 V d.c. and using the bodywork as cathode or anode, depending on the type of coating employed in this process. Regarding cathodic electrodeposition coatings, the positively charged molecules of the binding agent, the polymeric portion of the lacquer, are deposited on the surface of the negatively charged workpiece. Deposition and additional adsorption phenomena lead to a decrease of the amount of binding agent as well as neutralizing agent

(commonly a low-molecular-mass organic acid) in the basin during the coating process of a series of workpieces. To guarantee layers of reproducible thickness, it is very important to keep the concentration of the binding agent as well as the corresponding neutralization agent constant. Therefore, the composition of the basin contents has to be analyzed periodically. Another important aspect is the determination of ionic impurities. Because the workpiece has to pass a number of preliminary treatments before the coating procedure, ionic compounds may be carried into the basin. If the amount of these contaminants becomes too high, no more binding agent is deposited on the surface of the object to be coated, because (regarding systems with constant current) the transport of electric charge is taken over by these small ionic impurities. For this reason, it is important to monitor the amount of these analytes. The common method used is ion chromatography (IC), employing two separate runs for

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organic acids and inorganic anions or a gradient elution, both of which can be rather time consuming.

During the past years capillary electrophoresis (CE) has developed into a high-performance technique in analytical chemistry. Recently this methodology also became a viable alternative to IC for the determination of inorganic ions and other low-molecular-mass ionic solutes [2,3]. Beside the high-speed separation of standard mixtures of positively and negatively charged ionic solutes, more and more papers have been published on practical applications of CE for low-molecular-mass ionic compounds [4,5]. From the perspective of an alternative analytical technique, CE offers several advantages over IC: enhanced separation efficiency, tolerance of complex matrices and the separation mechanism of CE, which is distinctively different from the selectivity of IC, are well estimated attributes of this analytical method. One main practical benefit of CE is the fact that samples with extreme pH values or samples containing a large amount of organic substances may be analyzed more easily by CE than by IC. Compared to the corresponding chromatographic methods, CE offers the possibility of analyzing ionic solutes in complex matrices without extensive sample pretreatment. On the one hand, the excess of sample can be easily removed from the system by simply purging the capillary after analysis, on the other hand it is possible to introduce, for example, only the ionic compounds of the sample into the system by choosing a suitable injection method.

Compared to CE with UV-detection, devices equipped with conductometric detection offer significant enhancement in performance and sensitivity especially for the analysis of low-molecular-mass ionic compounds. A number of detector configurations suitable for both on-column and end-column detection have been reported in the literature [6–12]. Whereas in CE with UV-detection the suitability of a certain carrier electrolyte strongly depends on its UV-absorptivity, low-conductivity buffers or buffers suppressible with the common methods are used in the case of CE devices equipped with nonsuppressed or suppressed conductivity detection respectively. In nonsuppressed conductivity detection, the so-called Good's buffers [13,14] proved to be suitable carrier electrolytes for a number of separation problems [8–11,15,16]. Because the first commercially avail-

able CE device offering the possibility of conductivity detection has been introduced just recently [11], only a small number of papers dealing with the applicability of this system for the analysis of real samples has been published [11,15,16].

The aim of the present work was to demonstrate the suitability of CE combined with conductivity detection for the analysis of low-molecular-mass ionic compounds in difficult matrices like electrodeposition coating samples, including the study of the applicability of a variety of different carrier electrolytes for this purpose.

## 2. Experimental

### 2.1. Reagents and samples

All solutions were prepared from 18 M $\Omega$  high purity water obtained from a Milli-Q System (Millipore, Marlborough, MA, USA). Standard solutions were prepared by dissolving the appropriate salts or carboxylic acids (purity >99%).

Electrodeposition coating samples were homogenized by manual shaking for at least 10 min. For removal of the polymeric portion the lacquer was mixed with a 12-fold excess of an 0.01 M LiOH solution. Subsequently the sample was shaken for 15 min, filtered through a 0.45- $\mu$ m disposable filter cartridge, spiked with 200  $\mu$ l of a 500 mg/kg molybdate solution, used as internal standard and used for CE analysis.

A 0.1 mM solution of hexadecyltrimethylammoniumbromide (CTAB, Sigma, St. Louis, MO, USA) was used for purging the separation capillary to establish a reversed electroosmotic flow (EOF). Running buffers include the following electrolytes: 30 mM 2-(N-morpholino)ethanesulfonic acid (MES)–30 mM histidine (His) (pH 6.1), 25 mM 3-(N-morpholino)-2-hydroxypropanesulfonic acid (MOPSO)–15 mM arginine (Arg) (pH 7.0), 25 mM 3-[N-tris(hydroxymethyl)methylamino]-2-hydroxypropanesulfonic acid (TAPSO)–16 mM Arg (pH 8.0), 50 mM 2-(N-cyclohexylamino)ethanesulfonic acid (CHES)–30 mM Arg (pH 9.0) and 90 mM 3-(N-cyclohexylamino)-1-propanesulfonic acid (CAPS)–90 mM Arg (pH 10.0).

## 2.2. Electrophoretic separation

The CE instrument employed was a Crystal 310 (former Thermo CE, Franklin, MA, USA) equipped with a Crystal 1000 conductivity detector (Thermo CE) connected to a HP 3359 data acquisition system (Hewlett-Packard, Palo Alto, CA, USA). Separations were carried out using Con Cap I fused-silica capillaries (Thermo CE) with an effective length of 70 cm×50 μm I.D. Before analysis the capillary was rinsed with 0.1 mM CTAB solution for 0.5 min and running buffer for 3 min. Injection was performed in hydrodynamic mode at the cathodic side by applying a pressure of 25 mbar for 0.2 min. A potential of –30 kV was used for separation.

For comparative purposes, IC determinations were performed using a common IC system equipped with a 50-μl sample loop and a conductivity detector with suppression. Inorganic anions were analyzed in the ion-exchange mode using NaHCO<sub>3</sub>–Na<sub>2</sub>CO<sub>3</sub> as eluent, carboxylic acids in the ion-exclusion mode using 0.001 M octanesulfonic acid for elution.

## 3. Results and discussion

### 3.1. Selection of the carrier electrolyte

A number of carrier electrolytes, prepared from different aminosulfonic acids combined with α-amino acids, covering a pH range from 6.1 to 10 were investigated with respect to the analysis of anionic impurities (chloride, nitrate, sulfate and phosphate) as well as carboxylic acids (formate, acetate, oxalate, lactate and butyrate) commonly used as neutralization agents in electrodeposition coatings. All running buffers were prepared to give an identical background conductivity of 5.0–5.2 μS and with it similar ionic strength. Before analysis the capillary was rinsed with 0.1 mM CTAB solution for EOF reversal.

In Fig. 1 the electropherograms for a standard mixture containing 5 mg/kg of each investigated solute obtained with five different carrier electrolytes covering a pH range from 6 to 10 are shown. The MES–His (pH 6.1) buffer [8] and the MOPSO–Arg (pH 7.0) buffer proved to be less suitable for this analytical problem. No acceptable peak for phos-

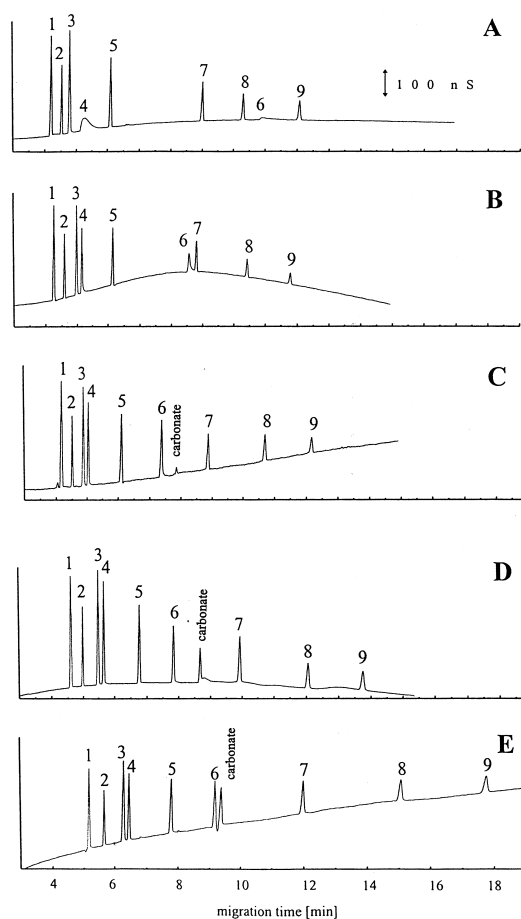


Fig. 1. Electropherograms of a standard mixture of inorganic and organic anions at a concentration level of 5 mg/kg each. Carrier electrolytes: (A) 30 mM MES–30 mM His pH 6.1 (B) 25 mM MOPSO–15 mM Arg pH 7.0 (C) 25 mM TAPSO–16 mM Arg pH 8.0 (D) 50 mM CHES–30 mM Arg pH 9.0 and (E) 90 mM CAPS–90 mM Arg pH 10.0; applied voltage: –30 kV; injection: 25 mbar for 0.2 min; capillary: 70 cm×50 μm I.D.; peaks: 1=chloride; 2=nitrate 3=sulfate; 4=oxalate; 5=formate; 6=phosphate; 7=acetate; 8=lactate; 9=butyrate.

phate could be obtained with either carrier electrolytes. Additionally, the peak shape for oxalate was poor, when the MES–His running buffer was used. The TAPSO–Arg (pH 8.0) as well as the CHES–Arg (pH 9.0) [W.R. Jones, unpublished results] carrier electrolyte yielded electropherograms with excellent resolution and peak shape for the analytes under investigation within a reasonable time of analysis. Increasing the pH to 10.0 by using the separation system based on CAPS–Arg led to a

decrease in separation efficiency. The peak obtained for phosphate and the one for carbonate which was present in all samples because of their high pH value were less resolved than in the case of the other carrier electrolytes.

All buffer systems mentioned above can only be used for CE combined with conductivity detection or direct UV-detection in the case of UV-absorbing analytes. A carrier electrolyte for the separation of anions, suitable for both conductivity as well as indirect UV-detection, based on a UV-absorbing negatively charged aromatic amino acid and a Good's buffer component serving as corresponding cation is currently being developed and will be presented in a future paper.

### 3.2. Analysis of electrodeposition coatings

Because of the promising results obtained with the 50 mM CHES–30 mM Arg (pH 9.0) running buffer, this system was chosen for the analysis of the coating sample. Both external calibration with and without addition of an internal standard (I.S.) were evaluated for quantitation of the selected analytes. Using molybdate as an I.S., standard deviations

obtained for the quantitation of the selected inorganic anions could be significantly decreased. Without the I.S., standard deviations calculated from four CE runs were between 3.2 and 4.6% for chloride, nitrate and sulfate and 13.9% for phosphate (the latter ion is present at levels of only 400  $\mu\text{g}/\text{kg}$ ). Using molybdate as I.S., standard deviations could be decreased to a range between 0.5 and 2.3% and 8.4% respectively. In the case of the analysis of carboxylic acids, no improvement of standard deviations was observed, when molybdate was used. Because of the results obtained for the inorganic anions investigated in this paper, we decided to use molybdate as I.S. for quantitation throughout this work. Fig. 2 shows the electropherogram of a standard mixture of small inorganic anions and carboxylic acids usually analyzed in electrodeposition coating samples. Concentrations of the analytes were chosen according to the common composition of the samples under investigation. This means that the amount of carboxylic acids, used as neutralization agents, greatly exceeds that of the inorganic anions. For this reason calibration curves were prepared between 1 and 10 mg/kg for chloride, nitrate, sulfate and phosphate, between 2 and 20 mg/kg for lactate and butyrate and

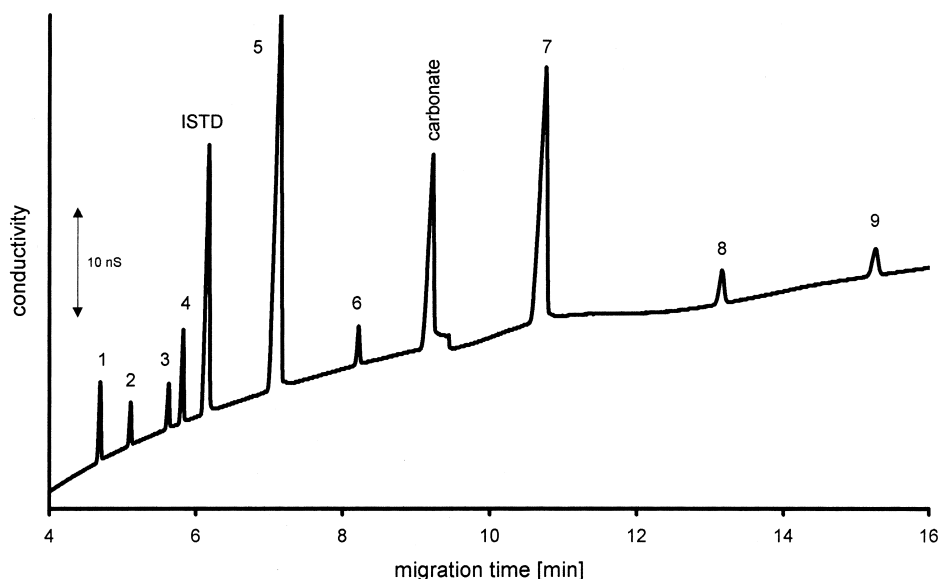


Fig. 2. Electropherogram of a standard mixture of inorganic and organic anions at concentration levels typical for electrodeposition coating samples. Carrier electrolyte: 50 mM CHES–30 mM Arg (pH 9.0); applied voltage: –30 kV; injection: 25 mbar for 0.2 min; capillary: 70 cm $\times$ 50  $\mu\text{m}$  I.D.; peaks: see Fig. 1.

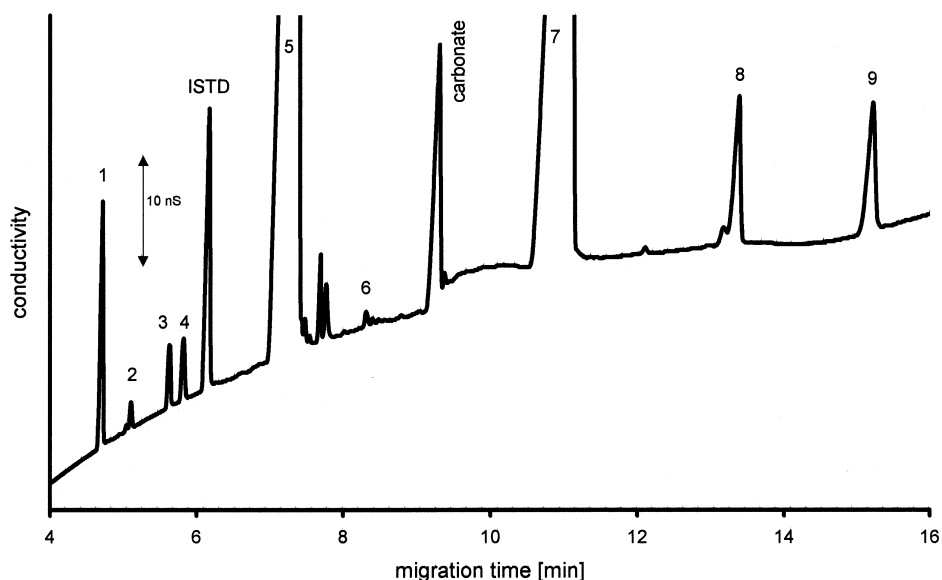


Fig. 3. Electropherogram of an electrodeposition coating sample. Conditions see Fig. 2.

20 and 200 mg/kg for formate and acetate. The correlation coefficients obtained for these calibration curves were better than 0.9995. Detection limits (LODs) increase with increasing migration times of the analytes. This is caused by the decreasing mobility of the solutes so that the difference between the conductivity of the analyte ion and the carrier electrolyte is decreased. LODs cover a range from 97  $\mu\text{g}/\text{kg}$  obtained for sulfate up to 571  $\mu\text{g}/\text{kg}$  for butyrate. Limits of quantification (LOQs) range from 161  $\mu\text{g}/\text{kg}$  for sulfate to 952  $\mu\text{g}/\text{kg}$  for butyrate.

An electropherogram obtained for a real sample (after dilution with 0.01 M LiOH solution to remove

the polymeric portion of the sample and filtration) is depicted in Fig. 3. The range of concentrations obtained for the selected analytes ranges from 0.4 mg/kg for phosphate to almost 200 mg/kg for acetate. Nevertheless, all solutes under investigation could be separated with a resolution sufficient for quantification. As can be seen from Table 1, good standard deviations could be achieved for three determinations of an electrodeposition coating sample (including sample pretreatment) and using the mean value of four consecutive CE runs for each sample. Comparing the data with those obtained by the more common IC technique, showed an excellent

Table 1

Comparison of the content of small anionic compounds in an electrophoretic coating sample obtained by CE AND IC

	Chloride	Nitrate	Sulfate	Oxalate	Formate	Phosphate	Acetate	Lactate	Butyrate	$t_{0.05}$
CE (mg/kg)	46	7	21	21	1512	4	1961	114	95	
R.S.D. (%)	2.4	2.7	1.2	0.3	1.4	3.3	1.8	1.9	9.3	
IC (mg/kg)	52	7	22	N.d.	1529	N.d.	1958	N.d.	N.d.	
$t_{\text{CE-IC}}$	6.4	1.0	0.7	—	1.2	—	0.0	—	—	2.78

Statistical comparison was performed using Student's *t*-test at 95% confidence level and four degrees of freedom.

N.d.=not determined.

agreement between the two methods. Only in the case of chloride slightly differing results could be observed as can be deduced from the  $t_{0.05}$  value.

#### 4. Conclusions

A number of carrier electrolytes was investigated for the analysis of small anionic contaminants and carboxylic acids used as neutralization agents in electrodeposition coatings by CE with an end-column nonsuppressed conductivity detector. A running buffer containing 50 mM CHES–30 mM Arg (pH 9.0) proved to be most suitable for this analytical problem. This separation system was selected for the analysis of real samples and validated by comparison with IC, the reference technique in this field of work. Good correspondence between the data obtained by both analytical methods could be observed. Therefore it can be stated, that the CE procedure described in this work provides reliable results within a shorter space of time than IC for the analysis of small ionic compounds in electrodeposition coatings.

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