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Notes

Direct Photometric Determination of Tungstate Ion in the Etching Solutions by Capillary Zone Electrophoresis

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In the determination of inorganic anions by capillary zone electrophoresis/indirect photometric method, chromate ion has been widely used as an indirect photometric reagent.[1-3] Although the method is applicable to any kind of analyte ions, there is sometimes serious baseline drift and/or relatively large baseline noise, because a UV-absorbing ion, a photometric reagent, exists in the migrating solution. On the other hand, a direct photometric method with less UV-absorbing migrating solution stabilizes the baseline, and is useful for particular UV-absorbing anions, which can improve the detection sensitivity.[4,5] The authors demonstrated highly sensitive determination of nitrate and nitrite ions with the direct method.[5] Some oxoacid anions were also detected.[6]

In this study, the authors aimed at determining tungstate ion sensitively, using the direct photometric detection and the stacking of analyte anions with a highly conductive electrolyte in the migrating solution. By the proposed method, tungstate in the etching solutions was well determined.

Experiment

Apparatus

An Applied Biosystems Model 270A-HT Capillary Electrophoresis System was used. A Hitachi D-2500 Chromato-Integrator was used for recording the electropherograms. A fused silica capillary, purchased from GL Sciences, was cut in the required length and attached to the system; the size of a capillary was 72 cm total length, 50 cm effective length to the UV detector and a 50 μm inner diameter.

Reagent

Oxoacid salts were used as received; they were K_2CrO_4, Na_2WO_4, $KMnO_4$, NH_4VO_3, $NaNO_2$, $NaNO_3$, $KBrO_3$, KIO_3, and Na_2MoO_4. Accurate amounts of these salts were dissolved in distilled water after drying under reduced pressure about 400 Pa at 50˚C. The migrating buffer components, such as acid base pairs of HCl–glycine, phosphoric acid–potassium dihydrogenphosphate, citric acid–NaOH and HCl–sodium monochloroacetate, were used. Sodium sulfate was used as a stacking reagent added to the migrating solution. All the reagents used were of guaranteed reagent grade. Water used was deionized and distilled once.

Procedure

A migrating solution containing 5 or 10 mM buffer (pH 3.2) and 0 – 30 mM sodium sulfate was poured into both a cathodic and an anodic reservoir, as well as into a capillary. The sample solution containing analyte anions was introduced into the capillary by a hydrodynamic injection from the cathodic end of the capillary. After that, a voltage was applied and electrophoresis was started. Analyte anions were photometrically detected at the anodic end of the capillary at 200 nm. Throughout the experiments, the capillary was held in a thermostated compartment kept at 30.0˚C.

For the determination of tungstate ion in practical samples, a migrating buffer containing 5 mM citrate buffer (pH 3.2) and 30 mM Na_2SO_4 was used.

Results and Discussion

Separability improvement by the addition of Na_2SO_4 in the migrating solution

The separation and determination of low-molecular-weight anions by capillary zone electrophoresis is performed by placing the detector on the anodic end of the capillary and by reversing or suppressing the electroosmotic flow (EOF) with a dynamic coating reagent[7] or by a chemical coating of the internal wall.[6,8] In this study, the authors adopted a low-pH migrating buffer, because of the good reproducibility of the migration time. Sodium sulfate was also added to the migrating solutions to suppress the velocity of EOF further. The

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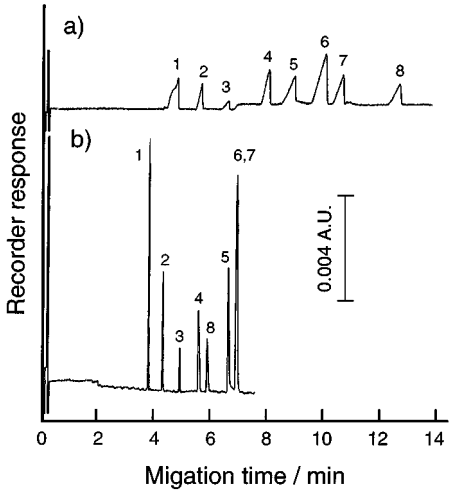

Fig. 1 Typical electropherograms for oxoacid anions in the absence and presence of Na_2SO_4. Sample: 1×10^{-4} M anions. Migrating solution: a) 5 mM citrate buffer (pH 3.2); b) 5 mM citrate buffer (pH 3.2)+30 mM Na_2SO_4. CE conditions: applied voltage, 20 kV; detection wavelength, 200 nm; capillary room temperature, 30°C; injection period, 3 s. Signal identifications: 1, NO_3^-; 2, MnO_4^-; 3, BrO_3^-; 4, CrO_4^{2-}; 5, WO_4^{2-}; 6, MoO_4^{2-}; 7, IO_3^-; 8, NO_2^-.

addition of sulfate ion can also enhance the stacking effect on analyte ions, and the signals for analytes can be sharpened.[5]

Typical electropherograms for 8 kinds of oxoacid anions are shown in Fig. 1. In Fig. 1 (a), obtained with a Na_2SO_4-free migrating buffer, the peak width of each analyte anion was broadened, and some of the signals were fronting ones. This was attributed to the low concentrations and small mobility of anions existing in the migrating solution, where the mobility of analyte anions was larger than that of migrating buffer component, citrate ion in this case. The migrating order of the oxoacid anions did not agree with the order of the zone mobility obtained at neutral or alkaline pH. This is because some of the analyte anions were present as their protonated forms in the low-pH migrating buffer.

In the electropherogram of Fig. 1 (b), obtained with a Na_2SO_4-contained migrating buffer, the oxoacid anions were found to be well separated and could be detected. Signals corresponding to their analyte anions emerged earlier than those obtained in the absence of Na_2SO_4, which led to a time-saving analysis. Further, the signals were well sharpened and leading of the peaks was depressed. Such results were caused both by the suppressed velocity of the EOF (*ca.* 1.0×10^{-4} cm^2 V^{-1} s^{-1}) compared with that in the absence of Na_2SO_4 (*ca.* 2.5×10^{-4} cm^2 V^{-1} s^{-1}) and by the stacking effect at the beginning of the electrophoresis. In the presence of Na_2SO_4 in the migrating buffer, the peak heights of the analytes increased to about 2.4-fold (CrO_4^{2-}) – 8.4 fold (NO_3^-), compared with those obtained in the absence of Na_2SO_4. Sodium sulfate concentrations from 10 mM to 30 mM were proved to be preferable for the present purpose: more stable and less noisy baseline and less time-consuming analysis. The migrating order of the analyte anions was somewhat different between (a) and (b) in Fig. 1. This difference seemed to be caused by an increase in ionic strength, which affects the acid dissociation property and the mobility of the analyte anions.

Effect of the components of migrating buffers on the detection of analyte anions

The effects of the components of migrating buffers on the detection of analytes were compared with each other, where the migrating buffers, such as 10 mM H_3PO_4–KH_2PO_4, 10 mM glycine–HCl, 10 mM citric acid–NaOH and 10 mM monochloroacetate–HCl, were investigated. Detectable analytes with each migrating buffer solution are summarized in Table 1. The baseline noise was relatively large with the 10 mM citric acid–NaOH buffer, because of the UV-absorption of citrate. The noise, however, was depressed to the same levels as to other migrating solutions by lowing the concentration of citrate to 5 mM.

In the phosphate buffer and the monochloroacetate buffer, WO_4^{2-} and MoO_4^{2-} could not be detected. This is because the reaction between analyte anions and migrating phosphate buffer components can produce heteropoly acids.[9] However, the effect of the monochloroacetate is not clarified. When the citrate and the glycine buffers were used, the detection of WO_4^{2-} was possible. The signal of WO_4^{2-}, however, disappeared in the presence of VO_3^- in the sample solution. This is also attributed to the formation of a heteropoly acid between WO_4^{2-} and VO_3^-. The reproducibility of the peak area of tungstate ion was the best when the citrate buffer was used. Therefore, the citrate buffer (5 mM) was adopted for the determination of tungstate ion.

Effects of the buffer components on peak shapes were also compared with each other. In the absence of

Table 1 Oxoacid anions detected with various migrating buffers[a]

Oxoacid anion	Migrating buffer[b]			
	Phosphate	Glycine	Citrate	Monochloroacetate
CrO_4^{2-}	○	○	○	○
MnO_4^-	○	○	○	○
WO_4^{2-}	×	△	○	×
MoO_4^{2-}	×	×	○	×
VO_3^-	○	○	×	○
NO_2^-	○	○	○	○
NO_3^-	○	○	○	○
BrO_3^-	○	○	○	○
IO_3^-	○	○	○	○

a. Concentration of anions in sample solution: 1×10^{-4} M.
b. Concentration: 10 mM, except for citrate; citrate: 5 mM.
Detection: ○, good; △, detected but less reproducible; ×, not detected.

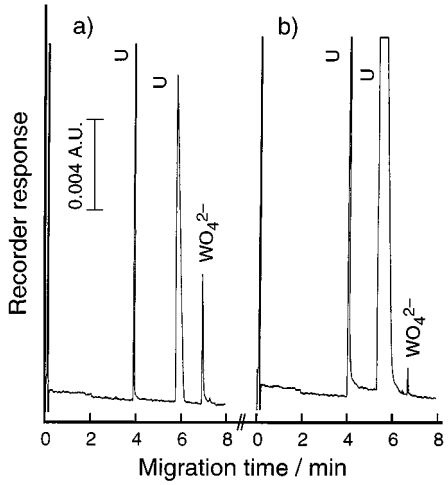

Fig. 2 Electropherograms for practical samples. CE conditions and migrating solution are the same as in Fig. 1 b). Sample (a) contains a larger amount of WO_4^{2-} than sample (b). U: unknown peak.

Na_2SO_4 in the migrating solution, the peak heights were largest when the phosphate buffer was used. However, the peak heights in the presence of Na_2SO_4 were almost identical for the buffers examined. The results also show that the anions can be stacked by adding Na_2SO_4 in the migrating solution.

Calibration graph and detection limits

A calibration graph for tungstate ion corresponding to the peak area showed favorable linearity in the concentration ranges from 10^{-6} to 10^{-4} M with the intercept of zero. The detection limit for tungstate ion at this stage was 5.0×10^{-6} M (1.2 ppm, S/N=3). Peak areas increased linearly with increasing the injection volume in the ranges from 3 s (9 nl) to 15 s (45 nl). The injection period of 3 s was selected from the viewpoint of sensitivity.

Application to the determination of tungstate ion in etching solutions of semi-conductors

The proposed method using the citrate buffer was applied to the determination of tungstate ion in silicon wafer etching solutions. The electropherograms for the practical samples are shown in Fig. 2. The pherograms show that the proposed method can be applied successfully to the analysis. The concentrations of tungstate ion were determined to be 1.4×10^{-4} M and 2.1×10^{-5} M for the samples (a) and (b), respectively.

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