Analysis of low-level anions in water extracts of hard disk drive heads by capillary electrophoresis

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Abstract

Analysis of anionic contaminants in various electronic components is of importance in assessing cleanliness as well as in identifying contaminants in failed devices. Typically the levels of anionic contaminants is in the low μg/l range. Capillary electrophoresis (CE) is one technique that can be used to analyze these low level anions. Analysis of several water extracts of failed devices as well as various components of the drive head and assembly was done using CE with analysis times of less than 5 min. Two different concentrations and pH values of a chromate-based electrolyte were evaluated. Both electrolytes achieved detection limits of less than 1.2 μg/l using an electromigrative injection.

Keywords: Hard disk drive leads; Buffer composition; Anions

1. Introduction

Ionic impurities on various electronic components can lead to several problems ranging from corrosion to higher resistivity on the device, either of which can lead to early failure or poor performance [1–3]. One type of component that is affected by these problems is hard disk drive heads. These small devices (typically a small metal square of less than 1 mm in length) are what actually reads information off the hard disk drive. These devices (known as sliders) are mounted onto a metal bracket (known as a suspension), which is placed onto several disk drives that make up a hard disk drive. The entire assembly, slider and suspension, is called a head gimbal assembly (HGA) and is shown in Fig. 1. These devices are extensively cleaned prior to assembly to remove ionic contaminants. Some ions of concern include chloride, nitrate, phosphate and sulfate. Currently, ion chromatography (IC) is the primary method used for analyzing ions from water extracts of disk drive heads. While this technique is

sensitive, it suffers from lengthy analysis times as well as the requirement for a pre-concentration step to analyze the anions.

Another technique that separates charged species is capillary electrophoresis (CE). CE separates
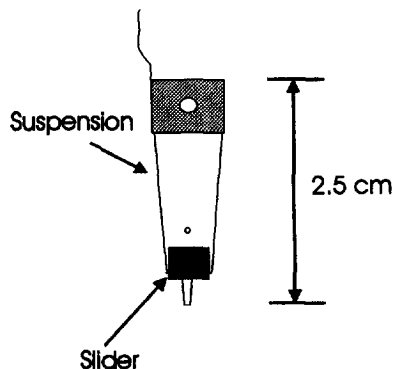

Fig. 1. Drawing of head gimbal assembly (HGA). The slider is a small metal piece attached at the bottom of the suspension near the bottom of the drawing. The slider is the part that actually is in contact and reads the disk drive. The overall size of the HGA is around one inch.

charged species on the basis of their mobility in an electric field (called electrophoretic mobility). Separation is therefore based on the ions charge-to-size ratio, thus providing an alternative selectivity to IC. Using CE techniques, simultaneous analysis of anions and organic acids is possible with analysis times of 5 min. CE has been successfully used for the analysis of anions in high purity water [4] and has been used also in other areas of the electronics industry. [5–9]

Analysis of these inorganic ions was done using a capillary electrophoretic technique that has been developed for the rapid analysis of low-molecular-mass inorganic and organic ions. For anion analysis, an osmotic flow modifier, OFM, is added to the electrolyte and reverses the normally cathodic direction of the electroosmotic flow (EOF) found in fused-silica capillaries. This creates a co-electro-osmotic condition that augments the mobility of the analytes. For low level (μg/l) analysis, injection of the sample is done by electromigrative enrichment. Electromigrative enrichment is a process where the capillary and electrode are immersed in the sample and a small voltage is applied to the sample. This process loads the anions onto the head of the capillary into distinctive bands based on their overall charge-to-size ratio. Two different chromate–OFM electrolytes were evaluated for the analysis of high purity water extracts of the hard disk drive heads.

2. Experimental

2.1. Instrumentation

The CE system employed was the Quanta 4000E Capillary Ion Analyzer (Waters, Milford, MA, USA). A Hg lamp was used for indirect UV detection at 254 nm. AccuSep polyimide fused-silica capillaries (60 cm×75 μm I.D.) were used throughout. Data acquisition and system control was carried out with a Waters Millennium 2010 Chromatography Manager with a SAT/IN module connecting the CE to the data station, with the signal polarity inverted from the CE. Software data processing in the Millennium software for CE data was done using the CIA software option.

2.2. Preparation of electrolytes

The chromate electrolyte used for indirect UV detection was prepared from a concentrate containing 100 mM sodium chromate tetrahydrate (Fisher Scientific, Pittsburgh, PA, USA). Osmotic flow modifier (OFM) for reversal of the direction of the EOF was a 20 mM concentrate (CIA-Pak OFM anion BT) obtained from Waters and converted from the bromide form into the hydroxide form by passing the OFM though an Alltech ion-exchange cartridge (Deerfield, IL, USA). The working electrolyte for indirect anion analysis consisted of either 10.0 mM chromate–1.5 mM OFM-OH electrolyte at a pH of 11.0 (electrolyte 1) or a 7.0 mM chromate–0.5 mM OFM-OH electrolyte at a pH of 8.0 (electrolyte 2). Sodium hydroxide was used to pH the electrolyte to 11.0 and boric acid was used to pH the electrolyte to 8.0. All working electrolytes were degassed prior to use. CIA methods are covered under US. Patents 5 104 506, 5 128 055, 5 366 601 and 5 156 724.

2.3. Chemicals

All ion standards were prepared from their salts and were of ACS grade or better. High purity water was obtained from a Milli-Q system (Millipore, Bedford, MA, USA). Volumetric plasticware was used for all standard preparation and plastic vials were used for sample extraction. All plasticware was soaked overnight in high purity water prior to analysis. Latex, non-powder, gloves (Fisher Scientific) and cleaned tweezers were used for all handling of the samples and extracts. High purity sodium octane sulfonate (VHG Laboratories) was used as an electromigrative additive and was added to all standards and sample water for extractions.

2.4. Calibration

Duplicate injections of standards at five different levels (2–40 μg/l) were performed in each electrolyte used. Time-corrected area was used for quantitation and a linear calibration curve was drawn. Table 1 shows the calibration data obtained using both electrolytes.

Table 1
Calibration information for the anions investigated

Anion	r^2	y-Intercept	Slope
Electrolyte 1			
Chloride	0.998	−8.643	79.139
Sulfate	0.997	49.332	56.418
Nitrate	0.998	−14.232	44.231
Oxalate	0.997	−6.902	46.833
Fluoride	0.996	−14.259	82.438
Phosphate	0.996	−11.884	28.642
Electrolyte 2			
Chloride	0.999	−29.107	49.188
Sulfate	0.999	27.688	33.111
Nitrate	0.998	−1.216	24.443
Oxalate	0.999	−5.723	26.641
Fluoride	0.996	−2.393	106.078
Phosphate	0.999	−10.317	18.651

2.5. Sample information

Samples of head gimbal assemblies (HGA) were obtained from various manufacturers of hard disk drives. Extracts of the drive heads (sliders), supsensions, or of the HGA assemblies were obtained by soaking and vortex-mixing the devices in 3.0 ml of a 70 μM NaOS solution for approximately 10 min. Water blanks were run prior to analysis. Typical contaminants found are chloride (1 $\mu g/l$ or less) and sulfate (2 $\mu g/l$ or less). This amount of sulfate present in the water blank contributes to the positive y-intercept found in the calibration curve. In the case of the samples analyzed using electrolyte 2, formate was found to be present in the water used for sample and standard preparation. For this reason, formate was not calibrated for these samples. Formate is a typical contaminant, along with chloride and sulfate, found in high purity water systems used at the bench. This is especially true in the case where the water is obtained directly from a municipal water system, without any prior clean-up.

3. Results and conclusions

Initial work in analyzing anions in the water extracts used a high pH chromate-based electrolyte (electrolyte 1) initially developed for the analysis of borate and silicate [4,9]. This electrolyte separates all major anions of interest in under 5 min, as shown in
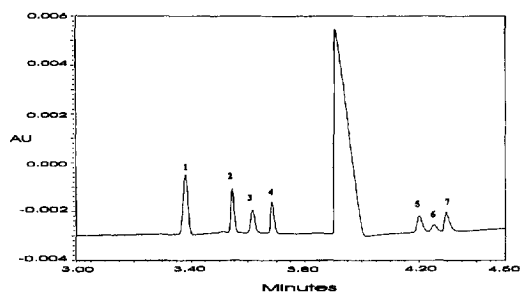

Fig. 2. Electropherogram of a standard. Conditions: fused-silica capillary, 60 cm×75 μm I.D.; voltage, 15 kV (negative); electrolyte, 10.0 mM chromate–1.5 mM OFM, pH=11.0; Indirect UV detection at 254 nm; electromigrative injection: −5 kV for 30 s Peaks: 1: chloride (8.0 $\mu g/l$); 2, sulfate (8.0 $\mu g/l$); 3, nitrate (8.0 $\mu g/l$); 4, oxalate (8.0 $\mu g/l$); 5, fluoride (2.0 $\mu g/l$); 6, formate (1.6 $\mu g/l$) and 7, hydrogenphosphate (8.0 $\mu g/l$).

Fig. 2, which is an electropherogram of a standard. The large peak at 3.90 min is carbonate, which is typically found due to the absorption of CO_2 in the sample. Using this electrolyte, analysis of two HGAs was done. Fig. 3 shows an electropherogram of a
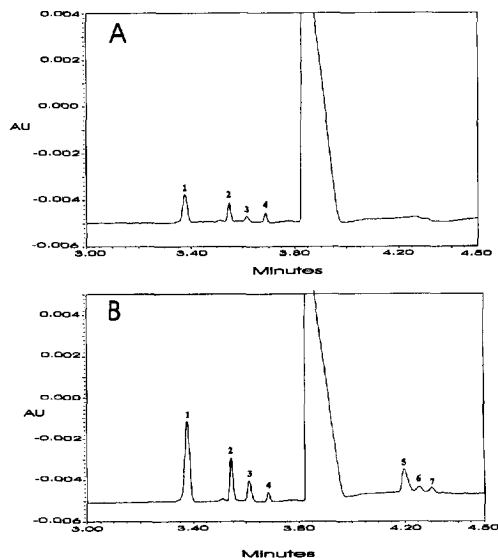

Fig. 3. Electropherogram of a typical head gimbal assembly (HGA) (A) and a simulated failed device that was not cleaned and was exposed to non-clean room air (B). (A), Peaks: 1: chloride (8.4 $\mu g/l$); 2, sulfate (4.3 $\mu g/l$); 3, nitrate (2.2 $\mu g/l$) and 4, oxalate (2.9 $\mu g/l$). (B), Peaks: 1, chloride (29.1 $\mu g/l$); 2, sulfate (11.7 $\mu g/l$); 3, nitrate (10.5 $\mu g/l$); 4, oxalate (6.5 $\mu g/l$); 5, fluoride (5.0 $\mu g/l$); 6, formate (2.6 $\mu g/l$) and 7, hydrogenphosphate (3.2 $\mu g/l$).

typical assembly (Fig. 3A) and Fig. 3B is an example of a simulated failed device that had not been cleaned and was exposed to standard laboratory air rather than a clean room and shows additional and higher levels of anions.

A second electrolyte (electrolyte 2) was evaluated for drive device analysis also. This electrolyte was evaluated because of the slightly different migration order of the anions of interest as well as the lower operating pH. Electrolyte 1 offers the ability to detect borate and silicate since it is at a higher pH, however, neither of the anions are present in these samples. Also, the storage life of the electrolyte is less at the higher pH, due to absorption of CO_2 which causes a lowering of the electrolyte's pH. Electrolyte 2, being at a lower pH, offers longer storage life for the prepared electrolyte (one week storage life for electrolyte 2 compared to one day for electrolyte 1). Fig. 4 is an electropherogram of a standard and shows the decrease in migration times of the later migrating peaks, with carbonate now migrating after the run is stopped. Analysis of several sliders and suspensions was carried out using this electrolyte. Fig. 5 shows the separation of a removed slider (Fig. 5A) and the assembly arm (Fig. 5B). Lower levels of anions are present on the slider than on the arm, which is expected and desired, since the slider is the part that is actually in contact with
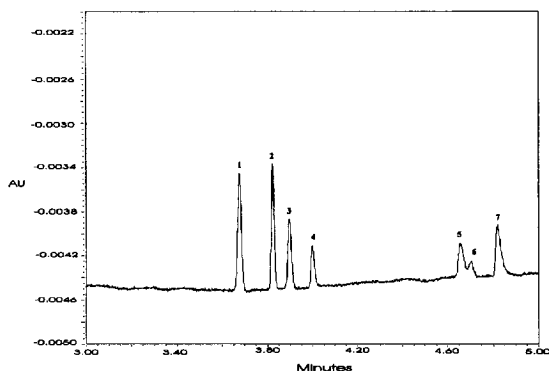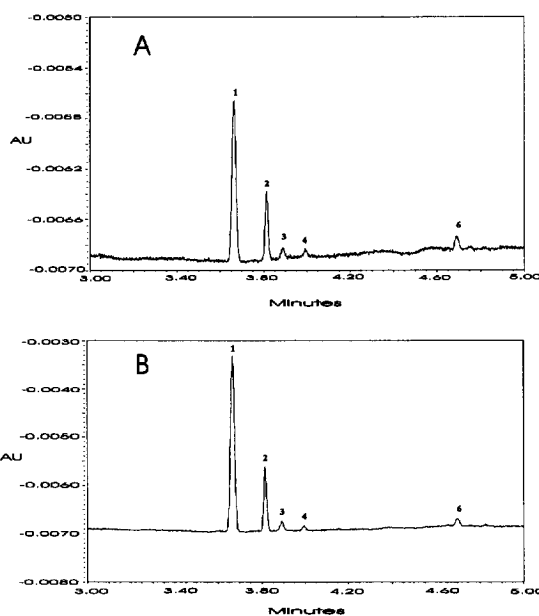

Fig. 5. Electropherogram of a slider sample (A) and the assembly arm that it was attached to (B). Conditions are as stated in Fig. 4. (A), Peaks: 1, chloride (9.4 μg/l); 2, sulfate (3.2 μg/l); 3, nitrate (0.9 μg/l); 4, oxalate (0.7 μg/l) and 6, formate (not quantitated). (B), Peaks: 1, chloride (25.9 μg/l); 2, sulfate (9.7 μg/l); 3, nitrate (1.9 μg/l); 4, oxalate (0.8 μg/l) and 6, formate (not quantitated).

the disk drive. Detection limits for the anions of interest using both electrolytes are given in Table 2. Noise was measured as peak-to-peak for 30 s of baseline near the analyte. Signal was defined as the distance between the average baseline and peak apex. For those anions that were present as contaminants in the make-up water (chloride and sulfate), the signals from those blanks were subtracted from the standard used for detection limit calculations. As seen, detection limits of 1.2 μg/l or better

Fig. 4. Electropherogram of a standard using electrolyte 2. Conditions: Fused-silica capillary, 60 cm×75 μm I.D.; voltage, 15 kV (negative); electrolyte, 7.0 mM chromate–0.5 mM OFM, pH=8.0; Indirect UV detection at 254 nm; electromigrative injection, −5 kV for 30 s. Peaks: 1, chloride (8.0 μg/l); 2, sulfate (8.0 μg/l); 3, nitrate (8.0 μg/l); 4, oxalate (4.0 μg/l); 5, fluoride (1.0 μg/l); 6, formate (1.0 μg/l) and 7, hydrogenphosphate (8.0 μg/l).

Table 2
Detection limits for the anions investigated[a]

Anion	Electrolyte 1	Electrolyte 2
Chloride	0.40	0.51
Sulfate	0.54	0.48
Nitrate	0.58	0.86
Oxalate	0.45	0.70
Fluoride	0.20	0.23
Phosphate	0.65	1.16

[a] amounts are in ug/l, S/N=3

Table 3
Repeatability data for anions investigated using electrolyte 2 (six replicate injections)

Anion	Migration time[a]	Peak area[a]
Chloride	0.17	2.10
Sulfate	0.14	2.22
Nitrate	0.17	2.79
Oxalate	0.19	2.19
Fluoride	0.17	4.88
Phosphate	0.27	4.68

[a]percentage relative standard deviation [R.S.D.(%)]

are possible using either electrolyte. Repeatability experiments of both migration times and area were performed using electrolyte 2 for a low μg/l standard (six replicate injections) and the results are summarized in Table 3. Reproducibility of better than 0.3% R.S.D. for migration times and 5% R.S.D. for peak area were achieved. Because of the increased storage life, electrolyte 2 offers the advantage of preparing large quantities of electrolyte. Electrolyte 1 does offer, however, the ability to analyze borate and silicate, as described in other papers [4,9].

4. Conclusions

As shown in the previous examples, CE can be used for the analysis of anion contaminants in hard disk drive heads. Analysis times of less than 5 min using either chromate electrolyte are possible with detection limits of 1.2 μg/l. Furthermore, electrolyte 2 offers the advantage of having a longer storage life, allowing for large quantities to be prepared and stored for daily use.

References

[1] R. Poliak, R. Matthews, K. Gupta, M. Frost and M. Triplett Microcontamination, June (1992) 45.
[2] M. Plat and J. De Leo, J. Chromatogr. 546 (1991) 347.
[3] E. Sacher, IEEE Transactions on Electrical Insulation, EI-18 (1983) 369.
[4] K. Gupta and S.H. Tan, Ultrapure Water, May/June (1994) 54.
[5] R.A. Carpio, R. Mariscal and J. Welch, Anal. Chem., 64 (1992) 2123.
[6] R.A. Carpio, P. Jandik and E. Fallon, J. Chromatogr. A, 657 (1993) 185.
[7] S.A. Oehrle, LC·GC, 14 (1996) 226.
[8] G. Bondoux, P. Jandik and W.R. Jones, J. Chromatogr., 602 (1992) 79.
[9] J. Krol, D. Cotter and M. Benvenuti, "Analysis of Borate and Silicate in Aqueous Matrices and High Purity Water Using Capillary Ion Analysis", presented at IC Symposium, Turin, 12–15 September, 1994.