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Ammonium extraction method for ion chromatographic measurements of disc drive components

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Abstract

The analysis of ionic micro-contamination is of growing importance in the disc drive industry. Through the use of ion chromatography, cleanliness of drive components can be assessed. An objective to improve quantification of highly reactive inorganic ions that exist within the drive environment was implemented. This paper presents a new extraction technique used to determine low levels of ammonium, by microbore ion chromatography. Various chemical compounds within adhesive formulations can be a source of extractable ammonium. By combining this new extraction method with ion chromatography, the percentage of different chemical compounds within adhesive formulations was correlated to the level of extractable ammonium observed. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

As disc drive parts are continually redesigned and specifications changed, part cleanliness must be maintained. Due to the high reactivity of ionic species, stringent specifications exist for anion and cation levels extracted from parts used in disc drives.

Ammonia readily reacts with acidic compounds to produce an ammonium salt [1]. Structural adhesives used in drive component parts can be a source of ammonia. Ion chromatography (IC) is a quick and efficient technique used to determine ionic species [2–4]. Ammonium can be separated from other cations and analyzed at the $\mu\text{g}/\text{l}$ level using IC [5]. This paper presents a novel methodology for analyzing extractable ammonium by the volatilization of

ammonia from drive piece parts and adhesive samples [6]. The samples undergo direct heating upon which ammonia is volatilized and reacted to form ammonium ion in a water solution. A method of similar scope was used to determine ammonia levels within stack gas flow from power plant boilers [7].

In this paper, we report a new extraction technique coupled with IC to determine low levels of ammonia from drive component parts and adhesives. This method was initially developed for a piece-part investigation and was later utilized to determine design criteria for an adhesive reformulation.

2. Experimental

2.1. Equipment

2.1.1. Ion chromatography equipment

All systems and components for ionic analysis

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were from Dionex (Sunnyvale, CA, USA). A Model DX-500 ion chromatograph equipped with a micro-bore pump and conductivity detector were utilized. An Ionpac CS12A (2 mm) main analytical column with a Ionpac CG12A (2 mm) guard column were used for the separation. A TCC-LP1 concentrator column was used to increase trace level sensitivity. Standard calibration range for ammonium ion was from 25 to 250 $\mu\text{g}/\text{l}$. A CSRS-II (2 mm) cation self-regenerating suppressor was used in the recycle mode.

2.1.2. Extraction system equipment

The extraction system entailed the use of a manifold with aluminum heating block from Seagate Technology (Shakopee, MN, USA). PTFE sample jars (240 ml) and PTFE tubing was supplied by Savillex (Minnetonka, MN, USA). Glass fritted impinger tubes, used as the extraction vessels were from Kimble Kontes (Vineland, NJ, USA). Tygon tubing and high-density polyethylene connectors were from VWR Scientific (Plainfield, NJ, USA).

2.2. Reagents

All reagents were of analytical-reagent grade unless otherwise specified. Deionized water at 18.2 M Ω cm resistivity, was used throughout. All ammonium standard solutions were prepared by diluting the standard Cation Mixture II (six cations, ppm level; Dionex). Methanesulfonic acid (high purity; Aldrich, USA) was used as the eluent. Eluent flow-rate was set at 0.25 ml/min.

2.3. Samples

Samples consisted of either disc drive parts with bonded structural adhesive or a cured adhesive coupon (typically a 1-g pellet).

2.4. Experimental set-up

The basis of the experiment was to heat adhesive samples (whether in part or coupon form) within a closed vessel, while an inert gas flows through the

sample jar and out to impinger extraction vessels. The exit gas flows through the sample jars to impinger tubes. Two impinger tubes were placed in series to measure potential breakthrough due to high ammonia concentrations. The gas flow entering the impinger tubes was bubbled through 18.2 M Ω water where soluble ionic species were retained.

2.5. Experimental conditions

The heater block temperature was set to 120°C while nitrogen gas flow measured at 100 ml/min from the impinger tubes (the gas line pressure was regulated at 20 p.s.i.; 1 p.s.i.=6894.76 Pa). A 20-ml volume of deionized water filled each impinger tube. The test duration was 5 h.

2.6. Experimental procedure

The procedure involves a detailed sample extraction followed by IC analysis. The sample extraction procedure starts by placing either a cured adhesive sample or component piece part within a PTFE jar (the test set-up allows for seven samples and one blank to be run simultaneously). PTFE tubing is used to connect the jar inlet and outlet lines to the manifold and impinger tubes. Next, the nitrogen gas flow is turned on and flow-rate is measured from the sample jar outlet. The manifold valve is adjusted so that the flow is set at 100 ml/min. Impinger tubes containing 20 ml of 18 M Ω deionized water are connected in series, where the first tube is connected to the second by Tygon tubing and polyethylene connectors. The sample jar outlet line is connected to the first impinger tube and the flow-rate is monitored again after the second impinger. Once all flows have been set and the impinger tubes are bubbling properly, the gas manifold and sample jars are lowered into the heater block and the temperature is set to 120°C.

When the temperature reaches 120°C, the samples are run for 5 h. After 5 h, the heat and nitrogen are turned off and both the manifold and sample jars are raised from the heater block. The sample extract from the impinger tubes is transferred into plastic vials and analyzed by IC.

3. Results and discussion

3.1. Principle

From the output chromatography, the concentration of ammonium extracted from the sample was determined. Whether the sample was present as a drive piece part or an adhesive coupon determined if the final data was reported as *per part* or *per gram*. A correction to the sample concentration was made by subtracting the ammonia concentration in the blank.

The following equations were used:

$$C_w = \frac{(S - B)V}{1000W} \text{ or } C_p = \frac{(S - B)V}{1000P}$$

where C_w is the concentration of ammonium in $\mu\text{g/g}$; C_p is the concentration of ammonium in $\mu\text{g/part}$; S is the concentration of ammonium in the sample in $\mu\text{g/l}$; B is the concentration of ammonium in the method blank in $\mu\text{g/l}$; V is the volume of sample extract in the impinger (ml); W is the mass of sample (g) and P is the per disc drive piece part.

If the level of ammonium found in the sample was at a higher concentration (outside of the 25–250 $\mu\text{g/l}$ calibration range), dilutions were made accordingly.

3.2. Experimental data

3.2.1. Effect of catalyst level

Adhesive types with varying catalyst component were assembled into drive piece parts and analyzed. Table 1 shows a positive correlation between % catalyst and level of extractable ammonium observed.

The level of extractable ammonium increased as the percentage of catalyst in the adhesive increased. Because these adhesive formulations showed levels

Table 1
Determination of ammonium in adhesives with varying % catalyst component ($n=3$)

Catalyst (%)	Average ($\mu\text{g/part}$)	SD ($\mu\text{g/part}$)
10	2.17	0.89
50	5.53	0.85
100	9.74	1.68

Table 2
Determination of ammonium in a catalyst and crosslinker ($n=3$)

	Average ($\mu\text{g/g}$)	SD ($\mu\text{g/g}$)
Catalyst	20.13	0.91
Crosslinker	14.67	6.11

above 1 $\mu\text{g/g}$, they were not further explored as an alternative to the current adhesive system.

3.2.2. Catalyst and crosslinker assesment

Samples of catalyst and crosslinker were analyzed for extractable ammonium content prior to addition to the other adhesive components (Table 2). It was important to determine if the catalyst and crosslinker contained an inherent level of extractable ammonium or if the ammonium extracted from the final adhesive construction was entirely a reaction by-product.

Both the catalyst and crosslinker contained extractable ammonia, suggesting that the level of ammonium in the finished adhesive constructions is due at least in part to the quantity of these materials used in the formulation.

3.2.3. Formulation assesment

A series of adhesives were studied to determine what combination of resin, crosslinker and catalyst, would yield lower levels of extractable ammonium. Table 3 shows the results from samples that were in adhesive coupon form (approximately 1-g samples).

The two adhesives that showed low levels of extractable ammonium (2B and 3B), had either no catalyst and crosslinker a or catalyst b with no crosslinker. Because of the low levels of extractable ammonium in adhesive 3B, catalyst b was pursued as a reformulation component for new experimental lots of adhesive.

Table 3
Determination of ammonium from adhesives with variable formulations ($n=3$)

Adhesive	Catalyst type	Crosslinker type	Average ($\mu\text{g/g}$)	SD ($\mu\text{g/g}$)
1B	a	a	21.32	1.51
2B	None	a	0.18	0.18
3B	b	None	0.00	0.01
4B	a	a	66.01	14.11

Table 4
Determination of ammonium in adhesives formulated with catalyst b ($n=3$)

Adhesive	Silica treatment	Catalyst type	Catalyst level	Crosslinker (%)	Average ($\mu\text{g/g}$)	SD ($\mu\text{g/g}$)
5B	a	1b	1	4	17.54	3.01
6B	a	1b	2	4	22.50	2.62
7B	a	2b	1	4	8.32	0.24
8B	a	2b	2	4	12.16	0.90
9B	a	1b	1	0	37.42	8.95
10B	a	2b	1	0	0.64	0.26
11B	b	1b	1	4	6.90	1.40
12B	b	1b	1	5	14.54	2.52
13B	b	1b	1	6	25.76	6.34
14B	b	2b	1	0.5	0.26	0.22
15B	b	2b	1	1	0.89	0.27
16B	b	2b	1	0	0.26	0.19

3.2.4. Developmental adhesive with catalyst b

Based on the data from the formulation assessment, the effects of five different variables were studied with respect to extractable ammonium levels. Table 4 shows 12 adhesives formulated with variations in the following: type of hydrophobic silica treatment, catalyst type, catalyst level, and crosslinker level. All adhesives were fabricated with one of two versions of catalyst b.

Four adhesives: 10B, 14B, 15B and 16B showed levels of extractable ammonium below $1 \mu\text{g/g}$. All four had catalyst 2b at level 1 with varying amounts of crosslinker. The adhesives with 0.5 and 1.0% crosslinker showed exceptional mechanical performance proving that these adhesives were good candidates for further investigation.

4. Conclusion

The ammonium extraction method proved to be a useful technique when used with microbore IC. The method provided accurate and precise determination of low concentrations of ammonium from drive components and adhesive samples. The procedure was repeatable, easy to set up and of low cost to design, due to the utilization of existing equipment.

From the method, specific chemical compounds within adhesive formulations were found to be a primary source of extractable ammonium. By combining this method with an adhesive reformulation experiment, new lots of application specific adhesives were designed. The adhesives that showed improved performance (both mechanical and low extractable ammonium), continue to be explored for use in future disc drive configurations.

References

- [1] D.D. Ebbing, M.S. Wrighton, in: General Chemistry, Houghton Mifflin, Boston, MA, 1990, p. 651.
- [2] N.E. Hoffman, Adv. Chromatogr. A 699 (1995).
- [3] P.R. Haddad, P.E. Jackson, Ion Chromatography – Principles and Applications, Elsevier, Amsterdam, 1990.
- [4] J. Weiss, Ion Chromatography, 2nd ed., VCH, New York, 1995.
- [5] H. Small, Ion Chromatography, Plenum Press, New York, 1989.
- [6] General Outgas Test Procedure by Dynamic Headspace Analysis, IDEMA Standard Document No. M11-99.
- [7] R. Dishakjian, Procedure for Collection and Analysis of Ammonia in Stationary Sources, US Environmental Protection Agency CTM-027, US Environmental Protection Agency, 1997.