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Analysis of anions in hydrofluoro ethers by ion chromatography

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Abstract

Hydrofluoro ethers (HFES) are considered to be an ideal cleaning solvent in applications like vapor degreasing and wet cleaning. It is also a good solvent replacement for CFCs (chlorofluorocarbons), HCFCs (hydrochlorofluorocarbons), HFCs (hydrofluorocarbons) and chlorinated solvents because they have a short atmospheric lifetime and low global warming potential. Based upon their properties, hydrofluoro ethers are ideally suited for the demands of the electronics industry. However, the electronics industry requires these solvents to have high purity, especially in the area of residual anions. This paper will present information on an extraction methodology for the transfer of anions from the hydrofluoro ether to water. Then, an analytical method utilizing ion chromatography that is capable of detection of 10 anions (fluoride, acetate, formate, chloride, nitrite, bromide, nitrate, sulfate, oxalate, and phosphate) in the part per billion level will be demonstrated.

Keywords: Hydrofluoro ethers; Inorganic anions

1. Introduction

In the electronics industry, there are a variety of cleaning and degreasing steps that need to be addressed. Many of the standard cleaning solvents have been shown to have high global warming potentials. One solution to the traditional CFCs, HCFCs, HFCs and chlorinated solvents has been hydrofluoro ethers (HFEs) [1,2]. These solvents have been shown to have a short atmospheric lifetime and low global warming potential. Correspondingly, use of hydrofluoro ethers is increasing within the electronics community. However, as electronics manufacturers utilize these products as cleaners or as a disk lube for hard disk drives, a standard concern is the amount of possible contaminant present in the solvent. Typical contaminants that may be monitored include trace metals, hydrocarbons and ions. It has been previously shown that trace levels of the ions chloride and sulfate can form trace levels of mineral acids and cause serious corrosion concerns [3]. Correspondingly, the utilization of ion chromatography to determine trace levels of anions on hard disk drive components has been utilized [4–7]. In addition, both the hard disk drive industry and semiconductor industry has highlighted the problems of residual anions in materials either through the publications of contaminant classifications [8] and or analysis standards which are required of all OEMs [9]. However, neither industrial group has presented methodology on determining residual anion levels in a hydrophobic fluid.

This paper will present and discuss a method for the extraction of anions from hydrofluoro ethers, specifically HFE 7100DL, and their analysis and quantitation by ion chromatography. The ions of interest in this project are fluoride, acetate, formate, chloride, nitrite, bromide, nitrate, sulfate, oxalate, and phosphate. The stability of the method will be shown through calibration curve stability and method spike recoveries. In addition, various extraction ratios of HFE 7100DL to water will be studied to determine if there is an impact of this ratio on the extraction process.

2. Experimental

2.1. Chromatographic system

All systems and components for ionic analysis were from Dionex (Sunnyvale, CA, USA). The hardware used for these analyses consisted of a DXC-500 ion chromatograph equipped with a GP40 gradient pump, a CD20 conductivity detector, an AS40 autosampler and an EG40 eluent generator. The eluent generator was used to generate KOH gradient concentrations. For all analyses in this report, the

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gradient profile consisted of the following: 0. 2 mM from 0 to 10 min, 0. 2 to 5. 0 mM from 10 to 15 min, and 5. 0 to 35 mM from 15 to 23 min. Eluent flow rates were set at 2. 0 ml/min with an injection volume of 4 ml.

For the analytical separation, an IonPac AG11 (50 mm × 4 mm) guard column and an IonPac AS11 (250 mm × 4 mm) analytical column were used. An IonPac trace anion concentrator TAC-LP1 (35 mm × 4 mm) was used for preconcentration. In addition, an ASRS-Ultra 4 mm suppressor was utilized in the recycle mode.

2.2. Reagents and samples

All reagents were of analytical reagent grade unless otherwise specified. The calibration standards were prepared from 1000 ppm anion stock standards purchased from Alltech Associates, Deerfield, IL, USA. Deionized water at 18 MΩ resistivity was used throughout.

The hydrofluoroether sample studied for this project was HFE 7100DL from 3 M (Maplewood, MN, USA). Sample types consisted of either pre-production research and development grade fluids or final production grade fluids. The HFE 7100DL was shipped to the laboratory in 4 l amber glass bottles, the same containers the material is sold in.

2.3. Extraction procedure

For most of the work in this study, a 2:1 ratio of HFE 7100DL (20 ml) to 18 M Ω water (10 ml) was placed in a 30 ml polypropylene Nalgene bottle (pre-rinsed 3–5 times with deionized water) and placed onto an orbital shaking apparatus for 2 h. After settling, the extraction water was pipetted from the sample container using a glass pipette and placed into a 5 ml sample vial (Dionex) for analysis. The vials and caps (without filter) were rinsed 3–5 times with deionized water prior to addition of the samples.

The ratio of HFE 7100DL to water was varied for the final experiment presented within this paper. For these ratio experiments, the amount of extraction water was always maintained at 5 ml, while the amount of HFE 7100DL was increased to reach the desired ratio. Polypropylene Nalgene bottles of various sizes were used for all sample extractions. Extraction samples were analyzed immediately following the extraction step and contained no preservatives or stabilizers.

2.4. Quality control parameters

All analyses within this report included a six-point linear calibration curve from 1 to 50 ppb for fluoride and chloride, 4 to 200 ppb for acetate (quadratic curve for acetate) and oxalate, and 2 to 100 ppb for all other analytes. The curves were not forced through zero. The lowest standard for each analyte was considered the limit of quantitation (LOQ) for this analysis.

Due to the low ppb level analysis of this method, blank samples were necessary in order to verify that there was no contamination in the system. Method blanks of the extraction water in the extraction vessels were prepared and analyzed in triplicate after the calibration curve but prior to the samples for every run. Continuing calibration blanks (CCBs) were run after every 10 injections and at the end of the analytical sequence to verify that the system operation was consistent. The blanks were required to show values at or below 2× the quantitation limit of the method.

An independent calibration verification (ICV) containing all 10 analytes was analyzed immediately after the calibration curve to confirm the accuracy of the calibrations. Continuing calibration verifications (CCVs) were run at least every 10 injections and at the end of the analytical sequence to verify consistent system operation.

Method spikes were prepared and analyzed in triplicate along with the sample. Extraction vials containing extraction water was spiked with a certified standard containing all 10 analytes. Matrix spikes were prepared and analyzed in triplicate along with the sample. Extraction vials, containing a sample were spiked with a certified standard containing all 10 analytes.

3. Results and discussion

3.1. Method analysis

The first question that arose when developing this ion chromatography method was if it was possible to create acceptable calibration curves in a production support analytical laboratory down to the low ppb levels for a large number of analytes. Table 1 lists the 10 analytes followed in this work, an r^2-value for these calibration curves, and the percentage difference of the curve from the actual value for the lowest calibration point. The results in this table show that it was possible to create calibration curves with a high degree of accuracy.

The next concern was whether or not these acceptable ion chromatography calibration curves could be consistently

Table 1
Calibration curves by analyte type

Analyte	Value for calibration curve (r^2)	Difference of curve value from actual value for lowest calibration level (%)	Lowest calibration level (ppb)
Fluoride	0. 997	19	1
Acetate	0. 995	22	4
Formate	0. 994	−29	2
Chloride	0. 997	−27	1
Nitrite	0. 995	−9	2
Bromide	0. 996	16	2
Nitrate	0. 997	16	2
Sulfate	0. 995	−20	2
Oxalate	0. 996	32	4
Phosphate	0. 999	0	2

Table 2
Method stability (initial calibration verification)

Analyte	Spike level (ppb)	Average recovery (%)	Standard deviation of recovery (%)
Fluoride	12. 5	105	13
Acetate	20	107	11
Formate	20	96	11
Chloride	25	97	13
Nitrite	25	95	10
Bromide	25	100	11
Nitrate	25	102	10
Sulfate	25	100	9
Oxalate	20	104	11
Phosphate	25	94	12

Average of 25 samples over 3 months.

generated over a long period of time. Over a period of 3 months, 25 separate analyses were run. Prior to sample analysis and just after the calibration curve was generated, an independent calibration verification standard containing all analytes was run. Table 2 lists the results for all 10 analytes, the standard level in ppb, the average percentage recovery and the standard deviation of this percent recovery. This table shows the characteristics of a very stable calibration system with average percentage recoveries close to 100% and low standard deviations (the highest being only 13%).

Now that stable and accurate calibration curves could be routinely generated, recovery of a known amount of the analytes from the extraction process needed to be demonstrated. Table 3 lists the matrix spike recoveries for a particular analysis. An extraction vial containing both the HFE 7100DL and extraction water was spiked with the 10 anions prior to the shaking process. The extraction vial was then carried through the normal extraction process. Recoveries were not <80% for any analyte (and most close to 100%) suggesting that the method did not have any major analyte loss mechanisms and that the method was an acceptable extraction method—at least from the point of view of analyte recovery.

Typical chromatograms of the samples analyzed for this paper are shown in Fig. 1 . Fig. 1A shows a water blank where the injection vial contained only the extraction water used in our laboratory. The lack of any chromatographic peaks above our quantitation level demonstrates that we do not have any interference in our system from the extraction water within our calibration range. The peak labeled 10 in Fig. 1A is carbonate, which is inherent in the system when utilizing the eluent generator with KOH. The presence of the carbonate peak did not interfere with the quantitation of any of the analytes. Peaks 3 and 4 correspond to formate and chloride, which were always present in water blanks at low levels, just below our quantitation level. Sometimes, the chloride background level could be higher than twice the quantitation level if adequate rinsing of the supplies was not done prior to extractions.

Table 3
Matrix spike recoveries

Analyte	Spike level (ppb)	Recovery (%)
Fluoride	12. 5	101
Acetate	20	95
Formate	20	80
Chloride	25	80
Nitrite	25	100
Bromide	25	95
Nitrate	25	90
Sulfate	25	87
Oxalate	20	91
Phosphate	25	92

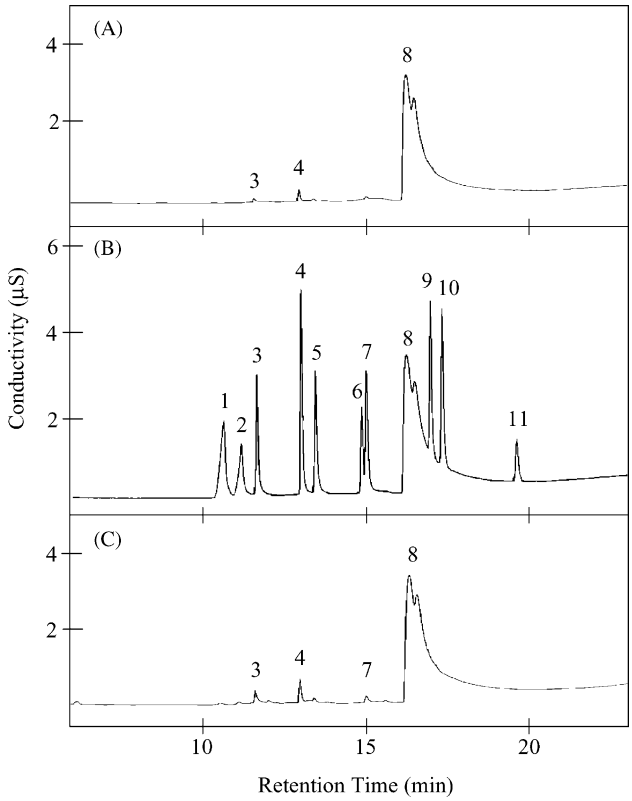

Fig. 1. Ion chromatographs with conductivity detection for: (A) a water blank containing only extraction water in the autosampler vial, peaks: 3, formate, 4, chloride, 8, carbonate; (B) a matrix spike of all 10 anions from this study at the concentrations listed in Table 3, peaks: 1, fluoride, 2, acetate, 3, formate, 4, chloride, 5, nitrite, 6, bromide, 7, nitrate, 8, carbonate, 9, sulfate, 10, oxalate, 11, phosphate; (C) a water extract of an extracted production sample of HFE 7100DL, peaks: 3, formate, 4, chloride, 7, nitrate, 8, carbonate.

Fig. 1B shows the chromatogram of the matrix spike containing all 10 analytes at the concentrations described in Table 3. In this matrix spike chromatogram, all 10 target analytes are present and are clearly chromatographically separated demonstrating the acceptability of this method. Finally, Fig. 1C shows the chromatogram of a water extract of a typical HFE 7100DL production sample where all analytes are present below the lowest calibration level (i. e., defined as our quantitation limit). However, there were trace background levels of formate, chloride, and nitrate (peaks 3, 4, and 7) just below quantitation levels.

Table 4
Effect of HFE:water ratio in extraction efficiency

Extractions ratio (HFE:water)	Analytes (ppb) extracted from original HFE sample			
	Fluoride	Acetate	Oxalate	Formate
20:1	3 ± 2	2 ± 0. 9	5 ± 1	5 ± 2
15:1	4 ± 0. 6	1 ± 0. 1	13 ± 0. 2	6 ± 0. 3
10:1	3 ± 1	8 ± 0. 4	10 ± 0. 9	3 ± 4
5:1	4 ± 1	12 ± 2	18 ± 4	4 ± 0. 8
2:1	5 ± 2	20 ± 7	24 ± 3	5 ± 0. 8
1:1	6 ± 1	20 ± 8	26 ± 0. 4	5 ± 1

3.2. *Effect of extraction ratio variation*

In an attempt to gain low detection limits in the reporting of residual anions in hydrofluoro ethers, one may be tempted to increase the ratio of HFE 7100DL to water in the extraction step. However, it will be shown that this can cause significant problems in the efficiency of the extraction process.

A pre-production, research and development HFE 7100DL sample, which was known to have some analytes present above detection limits, was extracted at various ratios with respect to the extraction water. These ratios varied from 20:1 to 1:1. The anions detected above quantitation levels in this particular pre-production HFE 7100DL sample were fluoride, acetate, formate and oxalate. All other anions were below detection limits for this particular HFE 7100DL sample.

Table 4 shows the amount of each anion extracted at the various extraction ratios. The HFE 7100DL samples were extracted in triplicate at the given extraction ratio, and the data in Table 4 lists the average extracted anion level in ppb and the standard deviation of the measurement. Fluoride and formate did not show any significant dependence on the extraction ratio. However, one finds that the acetate and oxalate show a significant dependence on the extraction ratio. The amount of extractable acetate from the HFE increases by a factor of around 10 as the extraction ratio decreases from 20:1 to 1:1, and extractable oxalate increases by a factor of around 5 with the same ratio decrease. This is probably due to nothing more than a decrease in efficiency of physical contact between the two fluids on the orbital shaker at the higher extraction ratios. The extraction ratios of 2:1 and 1:1 resulted in the largest detectable analyte levels, and there did not appear to be a significant difference between the results of the extraction ratios of 2:1 and 1:1. Therefore, an extraction ratio of 2:1 (HFE:water) was chosen as the ratio for the method as it yielded the high extraction values and it yielded detection limits two times lower than the 1:1 extraction ratio.

4. Conclusions

The anion extraction and analysis method for determination of residual anions in hydrofluoro ethers (HFE 7100DL) was shown to be an acceptable and stable method. The chromatographic peaks for all 10 analytes were clearly separated. The calibration curves showed stability over a period of a few months, and matrix spike recoveries were quite acceptable. In addition, it was shown that if one wants lower detection limits for this type of analysis, one cannot increase the ratio of HFE 7100DL to water during the extraction step. As the ratio of HFE 7100DL to water increases, the amount of extracted residual anion decreases quite rapidly which could lead to inaccurate analyses and underreported contamination values.

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