

Determination of anions in an epoxy curing agent by ion chromatography

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ABSTRACT

Within Martin Marietta's Analytical Services Organization (ASO), epoxy samples have traditionally been analyzed by high-performance ion chromatography (HPIC) using a bomb-prep method. Erratic sulfate results prompted an experimental 10% methanol preparation dissolution method to be used with subsequent analysis by HPIC. An HPIC method with isocratic separation and micro-membrane suppression is discussed in this paper. This method is specifically for the determination of sulfur as sulfate and fluoride in an epoxy curing agent. The new method will be used as a replacement for a current production laboratory bomb-prep HPIC method. Matrix interferences caused by Parr bomb (see *Oxygen Combustion Bombs, Bulletin 1100*, Parr Instrument, Moline, IL, USA) combustion products were eliminated using this method. A precision and bias study was done to document the effectiveness of the new method.

INTRODUCTION

In the past, plant processes have used adhesives that contain methylenedianiline (MDA). The Occupational Safety and Health Administration is in the process of setting new standards for the regulation of MDA, which has shown carcinogenic characteristics in laboratory tests on animals. Dr. G. F. Dorsey, a scientist in the Development Division of Martin Marietta Energy Systems, Oak Ridge Y-12 Plant (Oak Ridge, TN, USA), has invented a new curing agent. Tests conducted on this curing agent thus far have shown it to be non-mutagenic. The new agent may be suitable as a replacement for MDA, and it yields a product for polyurethane and epoxy resins used in adhesives, encapsulants, coatings, filament windings, and binders [1].

During the development of this epoxy curing agent, samples were submitted for ion chromatography (IC) characterization. Boron trifluoride

etherate, sulfuric acid, and sodium sulfate were used in the development process, and residual sulfur (analyzed as sulfate and calculated as sulfur) and fluoride were the anions of interest. IC analysis of the as-submitted epoxy product required a sample preparation step. The Parr-bomb preparation process is currently used for this type of matrix [2], but the procedure is technique-intensive and often gives erratic results (Table I). A preparation meth-

TABLE I
SAMPLE PREPARATION COMPARISON

Parr-bomb method		Methanol method	
Aliquot No.	Sulfur ($\mu\text{g/g}$)	Aliquot No.	Sulfur ($\mu\text{g/g}$)
<i>Initial preparation</i>			
1	610	1	53
2	< 50	2	63
		3	63
		4	63
<i>Rerun</i>			
3	52		
4	20		
5	< 20		

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od that is simple, fast and efficient was developed as a replacement. This method eliminates the problem of interfering ions in the sulfate analysis, which is caused by combustion products generated in the Parr-bomb preparation (Figs. 1 and 2). The desired fluoride anion analyses were also determined by this method.

EXPERIMENTAL

Apparatus

All chromatography was performed using a Model 2320i series Dionex ion chromatograph, with a 50- μ l sample loop. The system components consisted of one anion HPIC-AG-4A guard column (250 \times 2 mm I.D.), one anion HPIC-AS-4A separator column (250 \times 4 mm I.D.), an anion micro-membrane eluent suppressor (AMMS), a conductivity detector (CDM-1), and a gradient pump (GP). A concentration of 0.0125 M sulfuric acid regenerant was delivered to the AMMS by plumbing the "B" valve in conjunction with a pressurized 24-l container. The eluents were delivered to the columns by a Dionex eluent degas module (EDM).

Materials

Deionized ultrapure distilled water with a minimum conductivity of 15 M Ω · cm was used to make the eluents and regenerant. Reagent-grade sulfuric acid, sodium hydrogencarbonate, and sodium carbonate were used. The standard solutions were made using ultrapurity-grade sodium sulfate and sodium fluoride. Methanol, HPLC/spectro grade, was used as the initial solvent.

Eluent preparation

The eluent for fluoride analysis (0.0001 M NaHCO₃) was made by dissolving 21.0025 g of sodium hydrogencarbonate in 1 l of ultrapure water (stock eluent) and making a secondary dilution of 0.4 ml of stock solution to each liter of working eluent. The stock eluent for the sulfate analysis was made by dissolving 47.0456 g of sodium hydrogencarbonate and 47.6955 g of sodium carbonate in 1 l of ultrapure water. The secondary eluent (0.0028 M NaHCO₃–0.00225 M Na₂CO₃) was made by diluting 5 ml of the stock solution to each liter of working eluent [3].

Regenerant and standard preparation

The regenerant (0.0125 M) was made from reagent-grade sulfuric acid. The standards were prepared by diluting a 1000-ppm stock solution of sulfate and fluoride to make the working concentrations shown in Table III.

Flow-rates

The regenerant flow-rate was 2.5 to 3.0 ml/min. The eluent flow-rate was 2.0 ml/min.

Sample preparation

The unbombed samples were prepared by dissolving *ca.* 1 g of sample in 10 ml of methyl alcohol and diluting to 100 ml with ultrapure water. The final dilutions were made after filtering the emulsion through a 0.45- μ m Millex-HV filter.

RESULTS AND DISCUSSION

The initial step in the new preparation method is to dissolve *ca.* 1 g of the epoxy product in 10 ml of methanol. Boron trifluoride–methanol is a boron trifluoride soluble [4]. The residual sulfur in the epoxy products, as received for analysis, is present as a contaminant and is readily soluble. One aliquot is spiked, and deionized water is added to make 100-ml volume. After mixing, the solution is filtered through a Millipore Millex-HV 0.45 μ m filter unit, which is methanol compatible. This breaks up the emulsion and produces a clear solution that can be diluted and injected into the chromatograph. Spiked samples are taken through this preparation method to measure the recovery rates of fluoride and sulfate and to measure the precision of the method (Tables II and III). Parr-bombed samples are prepared as recommended [5]. The sulfate analysis scans obtained using the methanol preparation method were easier to interpret due to the absence of interfering peaks that are generated during the oxygen combustion Parr-bomb preparation method (Figs. 1 and 2). Fluoride results are acceptable when using either preparation method. Preparation time for the Parr-bomb method is *ca.* 1 h. Sample backlog delays of 1 or more weeks are common. The methanol preparation method is typically < 15 min. In both cases, the sample analysis time is < 10 min (not including preparation time).

TABLE II
PRECISION OF STANDARD ADDITION ANALYSIS OF EPOXY CURING AGENT

Concentration of spike (mg/l)	Calculated sample concentration (mg/l) ^a	Mean	S.D.	R.S.D. (%)
<i>Fluoride</i>				
0.00	6010			
0.20	6270			
0.40	5740	6010	334	5.6
1.00	6050			
<i>Sulfate</i>				
0.00	195			
0.20	172			
0.40	186	190	12	6.4
1.00	205			

^a All samples were diluted in order to match linearity range of standards at 3 μ S using an AS-4A column (Dionex).

TABLE III
STANDARD LINEARITY IN EPOXY MATRIX (METHANOL DISSOLUTION)

Fluoride		Sulfate	
Added (mg/l)	Recovered (mg/l)	Added (mg/l)	Recovered (mg/l)
0.20	0.17	0.50	0.55
0.40	0.37	1.00	1.00
1.00	0.95	1.50	1.40
2.00	1.80	2.00	1.72

CONCLUSIONS

IC analysis of an epoxy product, specifically boron trifluoride etherate, is possible after either Parr-bomb or 10% methanol-water preparation. The methanol preparation method is quicker and more efficient. The solution-filtration method relies less on the proficiency of the technician's technique than the Parr-bomb method. When using the methanol preparation method and the AS-4A column and eluent, IC analysis is straightforward, and the

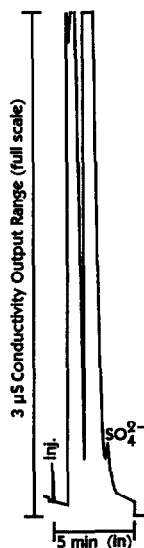


Fig. 1. Sulfate analysis with combustion product interferences. Conditions: Parr-bomb preparation sample, 2:1 diluted; columns, AG-4A and AS-4A; eluent: 0.0028 M NaHCO₃-0.00225 M Na₂CO₃; flow-rate, 2 ml/min.

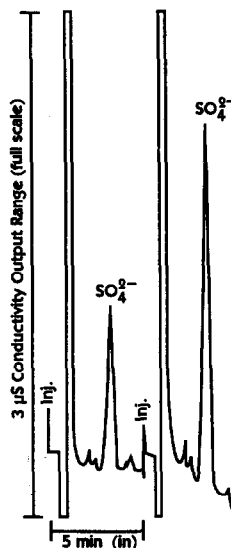


Fig. 2. Sulfate analysis after methanol preparation. Conditions: methanol preparation sample, 2:1 diluted + 0.50 mg/l sulfate spike; columns, AG-4A and AS-4A; eluent: 0.0028 M NaHCO₃-0.00225 M Na₂CO₃; flow-rate, 2 ml/min.

problem of interfering ions from the Parr-bomb combustion products is eliminated. Additionally, the cost of sample preparation associated with using the platinum-lined Parr-bomb is negated.

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