Dionex Case Study

Ion Chromatographic Methods for Quality Assurance Testing of Chloride and Sulfate in Ethanol

Linda Lopez, Dionex Corporation, Sunnyvale, California, USA

Customer: *Quality assurance group for a mid-sized independent ethanol producer*

Background

Biofuel producers must meet minimum standards for quality assurance before they can sell alternative fuels, such as ethanol, methanol or butanol. Sulfate and chloride are fuel contaminants found in alternative fuels and can potentially cause the corrosion of moving parts in vehicles and thus impact engine performance. US and European Regulatory agencies (for example, the ASTM and EN) have set limits for contaminants including sulfate and chloride in fuel ethanol; while Brazil, the world's largest fuel ethanol producer, has set what could be the most stringent limits on sulfate and chloride contamination in ethanol at 4 ppm and 1 ppm respectively.

Until now, quality assurance standards for fuel ethanol have used traditionally conventional analysis methods including potentiometric titration; however, new methods based on ion chromatography are quickly becoming the gold standard for the simultaneous separation and quantitation of inorganic ions (sulfate and chloride) in complex process mixtures. The IC methods have the advantage of showing good agreement with conventional analysis methods (potentiometric titration), and also show excellent reproducibility and recovery from complex matrices.

The quality assurance group for the mid-sized ethanol producer wanted a solution that would meet their requirements for repeatability, sensitivity, speed, and ease of use in an analytical method for quantifying sulfate and chloride in ethanol.

Challenge

The common standard operating procedures for the ethanol producer were based on wet chemical methods including potentiometric titration, which severely limited repeatability and reproducibility for the quantitation of soluble inorganic anions in fuel ethanol. For example, site-to-site and person-to-person variability plays a significant role in determining the correct values for solubility, method repeatability, and reproducibility. The titration method has many steps along its process that influence the test outcome, including weighing, mixing, solvent addition rate and method, and when to call the end point of the reaction. By contrast, ion chromatography can unambiguously determine the concentration of inorganic ions present in trace-level quantities (ppb – ppm range) in the presence of multiple co-eluting interferences.

Solution

A Dionex Corporation ICS-2000 Reagent-Free™ ion chromatography (RFIC™) system with AS40 autosampler and Chromeleon® Chromatography Data System software was installed to displace the titration equipment to determine soluble inorganic anions in fuel ethanol. The objective was to replace the time and labor-intensive titration method with a modern chromatographic method for quantitation of inorganic anions by direct injection on an AS14 column with suppressed conductivity detection. Another requirement for the Dionex methodology was to have the sensitivity (delivered by ion chromatography) to detect trace-level amounts of sulfate and chloride in the mixture.

Business Advantage

The key advantages of ion chromatography over potentiometric titration in this application was in achieving fast, reproducible results that required minimal sample preparation, the detection of trace-level inorganic anions, and ease of use for the analyst. The Dionex RFIC system provides QA/QC researchers the ability to ensure ASTM compliance of their fuel ethanol by permitting unambiguous determination of trace-level soluble anions of interest in the presence of multiple interfering compounds. The QA group manager said, "We need ultimate sensitivity to ensure we can meet the current ASTM specification for sulfate in ethanol. With regulations frequently changing, we want a fast, flexible solution capable of measuring total sulfate and chloride in concentrations as low as 1 ppm."

Another important benefit was the ease-of-use in sample preparation time. "The automatic eluent generation technology on the ICS-2000 RFIC system eliminates the need to manually prepare eluents, thus reducing variability in the analysis; We also save valuable time and effort that used to be wasted on preparing standards for our titration experiments," the QA manager said. Furthermore, for studies of this type where soluble anions are the target analyte, direct injection methods are often used, requiring little or no sample preparation when the analytes are present in their ionic, homogeneous forms. This, coupled with the low cost of operation requirements for RFIC with eluent generation, specifying only a reliable source of clean, deionized water, more than satisfied the quality assurance group's need for an easy-to-use, robust analytical solution.

Ion chromatography is fast becoming the preferred way to meet quality assurance standards for biofuel blends. Recently, the National Institute of Standards and Technology (NIST) along with the European Union and regulatory agencies in Brazil recommended the harmonization of standards for ethanol quality assurance based on analytical methods employing ion chromatography.

Dionex Ion Chromatography Systems

The Dionex ICS-2000 RFIC system combines innovative instrumentation, column chemistries, and Chromeleon software to quickly turn data into results. The system delivers a complete solution demonstrating superior sensitivity, speed, reproducibility and ease of use.

Dionex solutions are sought worldwide by researchers focused on increasing laboratory productivity and decreasing operational costs. Dionex maintains a worldwide profile with offices in the US, Austria, Australia, Belgium, Brazil, Canada, China, Denmark, France, Germany, India, Ireland, Italy, Japan, Korea, Singapore, Sweden, Switzerland, The Netherlands, and the United Kingdom. Distributors for Dionex also operate in Central and South America, South Africa, Asia, the Middle East, and elsewhere. Contact Dionex at 1228 Titan Way, PO Box 3603, Sunnyvale, California 94088-3603, USA, tel: 408 737 0700, fax: 408 730 9403

website: www.dionex.com.