Analysis of Chromium VI, Bromate, Nitrite and Nitrate Using a New Variable Wavelength Detector for the ICS-3000 Chromatography System

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ABSTRACT

Ion chromatography (IC) is commonly used to analyze drinking and waste water for common anions and cations. Suppressed conductivity detection is the most common detection method used for IC water testing. In addition to conductivity, absorbance detection can be used in conjunction with ion separation to provide more information per sample. Absorbance detection helps to decrease detection limits, acts as a confirmation to suppressed conductivity for certain analytes, or provides the primary means of detection for some non-conductive analytes or complex samples.

This presentation will illustrate the advanced absorbance capabilities of the ICS-3000 IC system when coupled with the new ICS-Series Variable Wavelength Detector (VWD). The combination of the ICS-3000 with absorbance detection allows the IC analysis of chromate in water, lowers the detection limit for bromate in drinking water, and can act as a confirmatory detection method for the concentration of nitrate and nitrite in drinking water.

INTRODUCTION

Chromium occurs in the environment primarily in two valence states, trivalent chromium [Cr (III)] and hexavalent chromium [Cr (VI)]. Exposure may occur from natural or industrial sources of chromium. The respiratory tract is the major target organ for Cr(VI) toxicity, for acute (short-term) and chronic (long-term) inhalation exposures. Shortness of breath, coughing, and wheezing were reported from a case of acute exposure to Cr(VI), while perforations and ulcerations of the septum, bronchitis, decreased pulmonary function, pneumonia, and other respiratory effects have been noted from chronic exposure. Human studies have clearly established that inhaled Cr(VI) is a human carcinogen, resulting in an increased risk of lung cancer. Cr (III), an essential element, is much less toxic than Cr(VI). The body can detoxify some amount of Cr(VI) to Cr(III). The general population is exposed to chromium [generally Cr(III)] by eating food, drinking water, and inhaling air that contains the chemical. The average daily intake from air, water, and food is estimated to be less than 0.2 to 0.4 µg, 2.0 µg, and 60 µg, respectively. Currently the U. S. Environmental Protection Agency (EPA) suggests a minimum contaminant level (MCL) of 100 µg/L, while the California MCL is 50 µg/L. When Cr(VI) is combined with diphenylcarbazide (DPC) it forms a purple-colored complex that can be measured quantitatively at 530 nm, as described in EPA Method 218.6.[1]

The analysis of common anions such as nitrite and nitrate can be done using IC. Some matrices with high ionic content, such as mineral water, brine, or wastewater sludge, may interfere with the accurate determination of nitrite or nitrate in the sample, so absorbance detection at 210 nm can be used confirm and/or quantify nitrite or nitrate.

Disinfection byproducts are formed when disinfectants used in a water treatment react with bromide and/or natural organic matter (e.g., decaying vegetation) present in the source water. Different disinfectants produce different types or amounts of disinfection byproducts. Disinfection byproducts identified in drinking water for which regulations have been established include trihalomethanes, haloacetic acids, bromate, and chlorite.* Bromate is a chemical that is formed when ozone used to disinfect drinking water reacts with naturally occurring bromide found in source water. The EPA has established the Stage 1 Disinfectants/Disinfection Byproducts Rule[2] to regulate bromate at an annual average of 10 µg/L in drinking water. This standard went into effect for large public water systems in December 2001 and for small surface water and all ground public water systems in December 2003. EPA methods 300.1, 317.0 and 326.0[3-5] have been established to allow accurate determination of 10 µg/L bromate. Bromate can be determined by either suppressed conductivity or absorbance detection IC. To achieve superior detection limits (as in EPA Method 317.0), bromate is reacted with a post-column reagent and the product is detected at 450 nm. Combined, these detection methods can be used as primary and confirmatory analysis techniques.

* A glossary of disinfection byproducts can be found on the EPA website in the Water section or at http://www.epa.gov/enviro/html/icr/gloss_dbp.html.

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DISSCUSSION

The addition of the ICS-series VWD Variable Wavelength Detector to the ICS-3000 IC system increases application flexibility by offering a wider range of methods.

IC methods are used for the determination of common anions and cations in drinking and waste water samples. Suppressed conductivity is used for many of these analyses, but can be subject to matrix interference or unacceptable method detection limits. Bromate detection limits can be significantly lowered when the ion is reacted with *O*-dianisidine (ODA) and detected in the visible range. Nitrate and nitrite ions can be confirmed and quantified directly in the ultraviolet range of detection. Hexavalent chromium cannot be detected to required detection limits by suppressed conductivity, and therefore IC methods must use postcolumn reagent delivery and absorbance detection. Other ions that can be detected by absorbance following an ion-exchange separation include silica, transition metals, metal cyanide complexes, nucleotides, and bromide.

Equipment

- AS Autosampler
- DP Dual Pump
- TC Thermal Compartment
- VWD Variable Wavelength Detector

Figure 1. The ICS-3000 system with ICS series VWD.

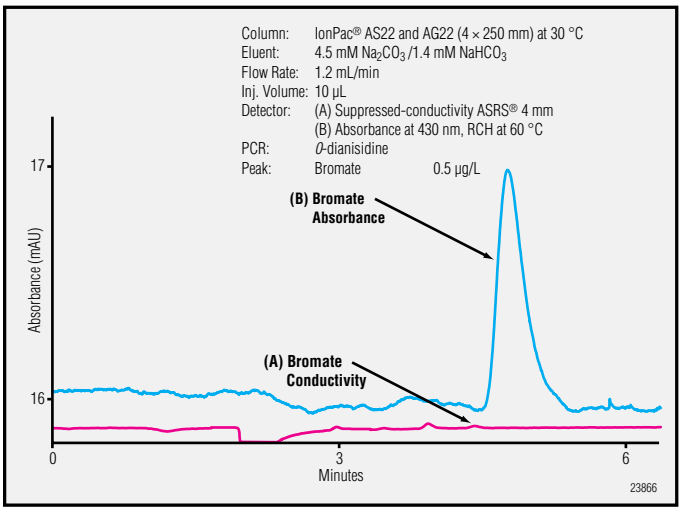

Figure 2. Suppressed conductivity detection for bromate compared to absorbance detection of bromate at 430 nm after addition of post column 0-dianisidine.

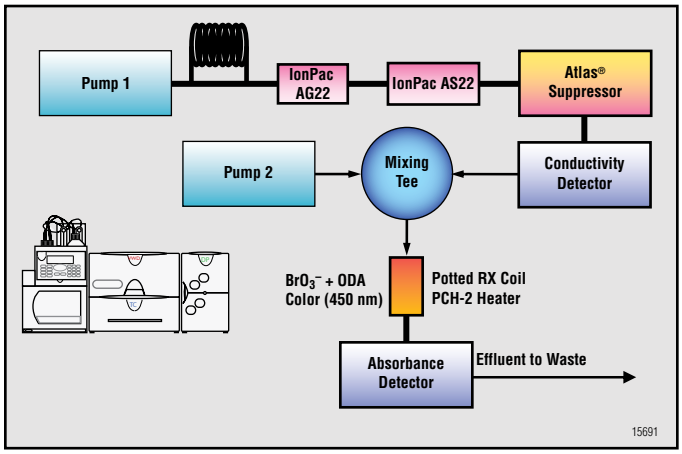

Figure 3. Schematic of an IC system with suppressed conductivity and post column reaction with absorbance detection according to U.S. EPA Method 317.0.

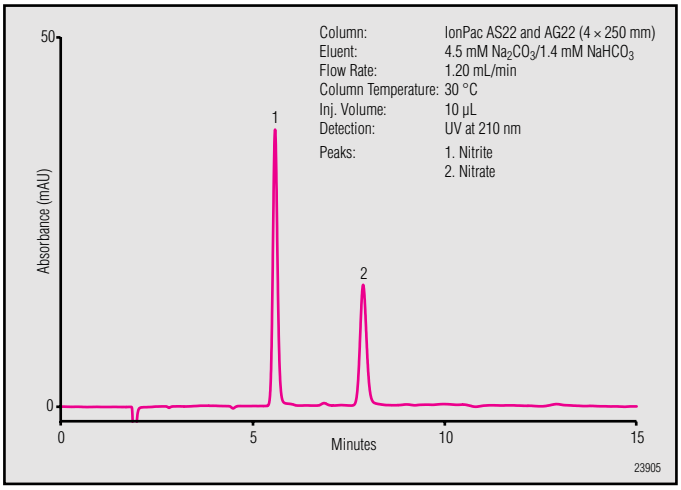

Figure 4. Selective determination of nitrite and nitrate in drinking water using an IonPac AS22 4 × 250 mm column.

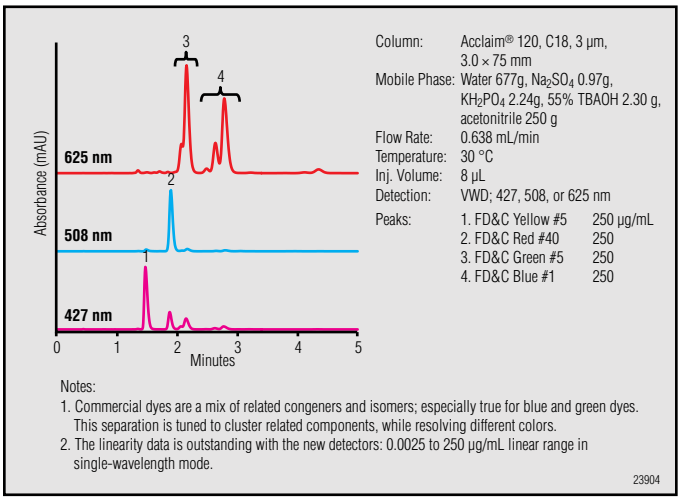

Figure 5. Separation of a commercial dye mixture with multiple wavelength detection.

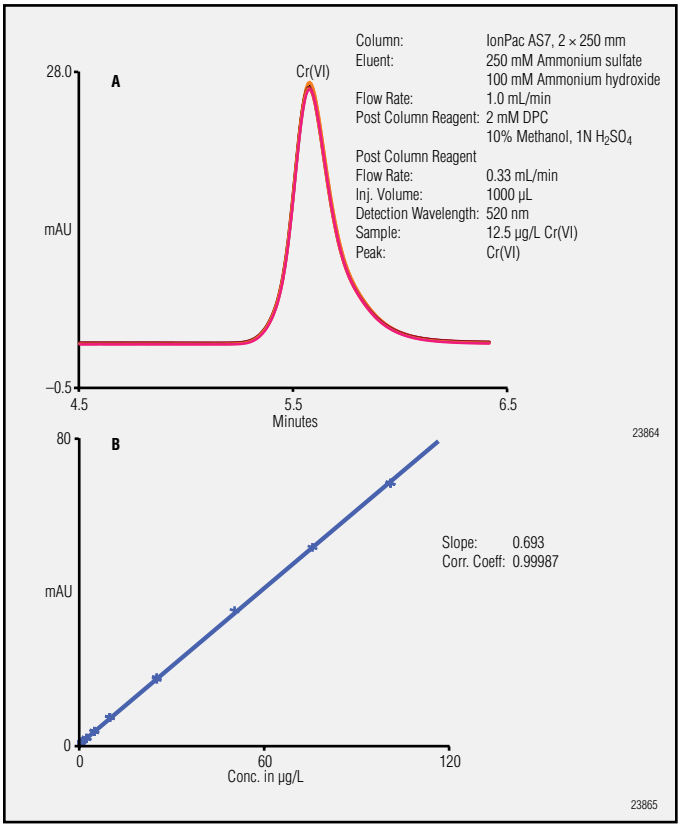

Figure 6. Detection of hexavalent chromium. (A) Precision of Cr(VI) over 10 runs and (B) calibration curve of Cr(VI) concentrations ranging from 0.1 µg/L–100 µg/L.

Figure 7. VWD/TC detail.

VWD Benefits

- Monitor four wavelengths simultaneously for superior analysis of complex mixtures.
- Broad detection range, 180–900 nm, enables detection of more compounds.
- Expanded linear range delivers accurate detection of concentrated and dilute samples.
- Excellent signal-to-noise improves minimum detection limits.

TC Benefits

- Increased flexibility with single or dual valves for handling complex applications.
- Expanded temperature range allows a wide variety of applications.
- Integrated column chip technology tracks column life for greater reliability.

CONCLUSION

The conductivity and absorbance capabilities of the ICS-3000 system allow a wide range of analytes to be analyzed by IC. With the addition of highly-sensitive absorbance detectors, analytes that are not detectable with normal suppressed conductivity can be easily analyzed. Analytes that may be susceptible to matrix interference when performing typical IC can easily be confirmed by adding an absorbance detector in-line after the conductivity cell. Detection limits for some weakly-conducting ions can easily be lowered by the addition of post-column chemistry and absorbance detection. For some important ions, absorbance detection can enhance typical ion chromographic methods.

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