Determination of Trace-Level Perchlorate by IC–MS-MS Using U.S. EPA Method 332.0

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Perchlorate has received widespread attention as an environmental pollutant over the past several years. Perchlorate was most recently monitored for occurrence in drinking waters under U.S. EPA's first Unregulated Contaminated Monitoring Rule (UCMR) using an ion chromatography (IC) suppressed conductivity detection technique according to the procedural requirements of EPA Method 314.0. Based on the monitoring data collected during UCMR, the U.S. EPA proposed a regulatory limit for perchlorate in drinking water of 1 mg/L. In addition, new methods capable of reliable determination of perchlorate safely below this limit have been developed by U.S. EPA, including Methods 314.1, 331.0, and 332.0. Method 332.0 relies on an IC separation with either mass spectrometry (MS) or tandem mass spectrometry (MS-MS) for detection and quantitation. This application note demonstrates the use and advantages of IC–MS-MS per Method 332.0 (1).

Experimental

A Dionex ICS-2500 IC equipped with a matrix diversion valve and auxiliary pump was coupled to an Applied Biosystems/MDS Sciex API 2000™ MS-MS and used to demonstrate Method 332.0. Three Multiple Reaction Monitoring (MRM) transitions were monitored to quantify the perchlorate anion in drinking water samples: $^{35}Cl^{16}O_4^-$ (*m/z* 98.8)/ $^{35}Cl^{16}O_3^-$ (*m/z* 82.8), $^{37}Cl^{16}O_4^-$ (*m/z* 100.9) / $^{37}Cl^{16}O_3^-$ (*m/z* 84.8), and $^{35}Cl^{18}O_4^-$ (*m/z* 107.0) / $^{35}Cl^{18}O_3^-$ (*m/z* 89.0). The last transition is for the Oxygen-18 stable isotope internal standard used in this method. The isotopic ion ratio of $^{37}Cl/^{35}Cl$ (10,000/3610 = 3.16) was used to further confirm the presence of Perchlorate and to detect any coeluting isobaric interferences. The minimum detection limit (MDL) of perchlorate in reagent water in these experiments was determined to be 0.004 µg/L using MRM 98.8/82.8 and a 100-µL injection. Linear calibration was typically performed from the MDL up to approximately 10 µg/L.

Result and Discussion

Figure 1 shows the measurement of perchlorate near the detection limit at 0.005 µg/L. MRM is a standard technique for quantitative LC–MS-MS analysis and performs equally well in IC–MS-MS. It uses pairs of target precursor ions and unique fragment ions for quick quantification of target species. This approach has been used in many pharmaceutical and environmental applications to generate unmatched limits of detection or quantification, precision, and accuracy. Diversion of the high total dissolved solids (TDS) matrix anions away from the MS-MS while eluting from the IC results in robust method performance. This IC–MS-MS method has been successfully tested under high TDS matrix conditions of 1800 mg/L each of carbonate, sulfate, and chloride for extended periods. The MRM lowest concentration minimum reporting limit (LCMRL) as determined by the protocol outlined in Method 332.0 during a Second Laboratory Validation study (SLV) for the U.S. EPA was approximately 0.0157 µg/L. IC–MS-MS has not only been successfully used for analysis of drinking water, but also to test for perchlorate in a wide variety of environmental and food samples. A broad selection of food products such as fresh fruits and vegetables, milk, alcoholic beverages, baby foods, juices, and bottled water that had been harvested or processed in many parts of the world were analyzed. The levels of perchlorate found ranged from 0.047 ± 0.006 µg/L to 463.50 ± 6.36 µg/L using MRM 98.8/82.8 and a 100-µL injection. The MRM experiments and the isotopic ion ratio of $^{37}Cl/^{35}Cl$ employed by this IC–MS-MS method guarantee the analyst reliable, interference-free determination of perchlorate.

References

(1) "Determination of Perchlorate in Drinking Water by Ion Chromatography with Suppressed Conductivity and Mass Spectrometric Detection" (U.S. Environmental Protection Agency, Cincinnati, Ohio, Method 332.0, 2005).

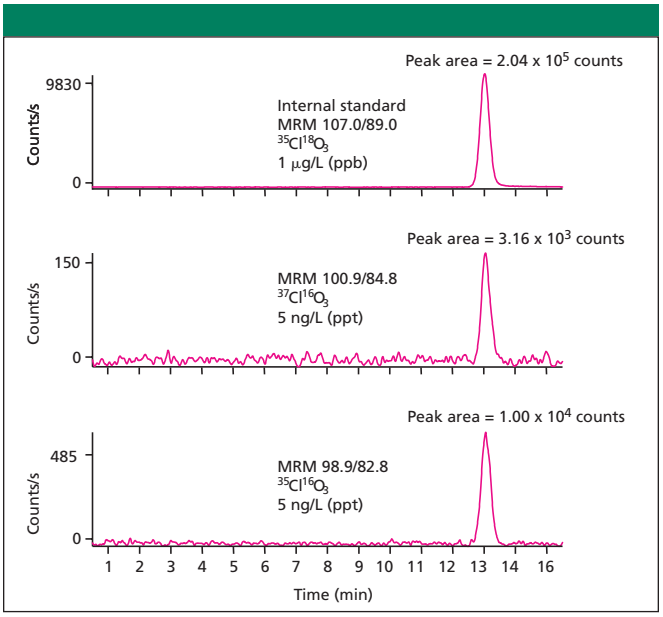

Figure 1: Determination of 0.005 µg/L perchlorate in a 100-µL injection of reagent water by IC–MS-MS with an Oxygen-18 enriched perchlorate isotopic internal standard (1 µg/L).

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