

Determination and Quantification of Perchlorate in a Fruit Matrix Using Accelerated Solvent Extraction and IC-MS

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Overview

Purpose: Our goal was to develop a total workflow solution for extracting, determining and quantifying perchlorate in a complex fruit matrix. We sought to maximize sample throughput while retaining low ppb level sensitivity.

Methods: Strawberry samples were spiked with perchlorate followed by accelerated solvent extraction technique and analyzed using ion chromatography coupled with mass detection.

Results: We demonstrate a sensitive and robust method for monitoring perchlorate levels in strawberries with reduced sample preparation time and labor.

INTRODUCTION

Perchlorate is an oxidizing agent used in munitions and firework manufacturing that has been identified as an environmental contaminant of water, soil, and food crops (Fig. 1). Sufficiently high doses of perchlorate can inhibit iodide absorption in the thyroid, leading to metabolic disruption with effects on fetal and infant development. Consequently, the US EPA and FDA have developed chromatographic methods for its routine monitoring in water and food crops. Unlike its analysis in drinking water, which requires minimal sample preparation, perchlorate determination in fruit and vegetable matrices presents considerable challenges due to high levels of interfering matrix ions; these are particularly problematic when quantifying at typical parts-per-billion (ppb) concentrations. In addition, food samples require laborious extraction procedures that limit throughput and reduce precision due to variable handling. The use of accelerated solvent extraction and ion chromatography coupled with mass spectrometry (IC-MS) presents a complete workflow solution that minimizes sample preparation and maximizes sensitivity for perchlorate in foods (Fig. 1). Mass detection reduces the need for post-extraction clean-up procedures through added selectivity relative to conductivity detection. Moreover, the Thermo Scientific™ Dionex™ ASE™ Accelerated Solvent Extractor System increases sample-to-sample consistency and lab productivity. Altogether, these data highlight a simplified method for reliable monitoring of ppb-level perchlorate in fruits and vegetables.

MATERIALS AND METHODS

Sample Preparation

Extractions were performed using 1 g of local, store-bought strawberries blended with 5 g of diatomaceous earth per 34 mL Dionex ASE 350 Vial. Assembly of the Dionex ASE Vial from bottom to top: two layers 30 mm glass fiber filter (GFB), 6 g basic alumina powder (Sigma Aldrich), 1 layer GFB, remainder of vial is filled with blended sample. Samples were spiked with 10 ppb perchlorate (99 m/z) standard pre-extraction for recovery analysis. A Dionex ASE 350 instrument was used for all extractions using 18 MΩ water as solvent with the following method parameters: Pressure (1500 psi), Temperature (80°C), Equilibration (5 min), Static (5 min), Flush (30%), N₂ Purge (120 s), and Cycles (3). Samples were collected using 65 mL collection vials and diluted to a final volume of 45 mL.

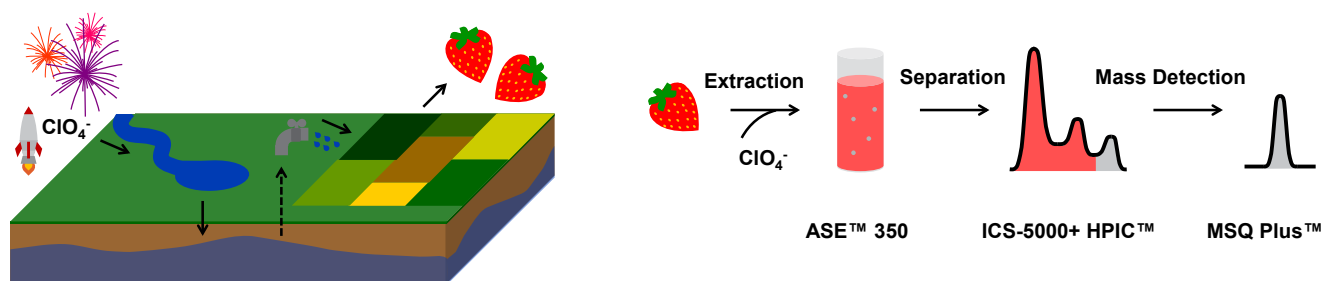
Ion Chromatography and Mass Spectrometry

A Thermo Scientific™ Dionex™ ICS-5000+ instrument configured in external water mode was used for chromatographic separation of perchlorate from the strawberry matrix. The instrument was configured with a Thermo Scientific™ Dionex™ IonPac™ AS16 2x250 mm column, Dionex IonPac AG16 2x50 mm Guard, Thermo Scientific™ Dionex™ AERS™ 2 mm Suppressor and a 100 µL sample loop. Each sample was spiked with 10 ppb perchlorate internal standard (107 m/z; ISTD) prior to analysis. Sample injections were performed in push full mode and separated over a KOH gradient from 0.5 mM-100 mM spanning 30 minutes. 50:50 H₂O:ACN was teed into the column effluent prior to entering a Thermo Scientific™ MSQ Plus™ Single Quadrupole Mass Spectrometer to aid desolvation.

Data Analysis

All instrument control and data processing were performed using Thermo Scientific™ Dionex™ Chromeleon™ 7.2 SR3 Chromatography Data System software.

FIGURE 1. Environmental perchlorate and its analytical workflow.



RESULTS

A perchlorate stable-labeled internal standard (ISTD) (107 m/z) was used for perchlorate quantification by monitoring its response ratio with natural perchlorate (99 m/z). Both analytes exhibited similar retention and coeluted at identical times in the chromatogram (Fig. 2). Using selected ion monitoring (SIM) mode of the MSQ Plus Mass Spectrometer, both masses were analyzed in a perchlorate calibration curve performed in blank strawberry matrix (Fig. 2). Calibration was calculated with seven levels ranging from 1-100 ppb natural perchlorate while the concentration of the ISTD was held constant at 10ppb.

FIGURE 2. Perchlorate calibration curve using selected ion monitoring (SIM) and an internal perchlorate standard (ISTD).

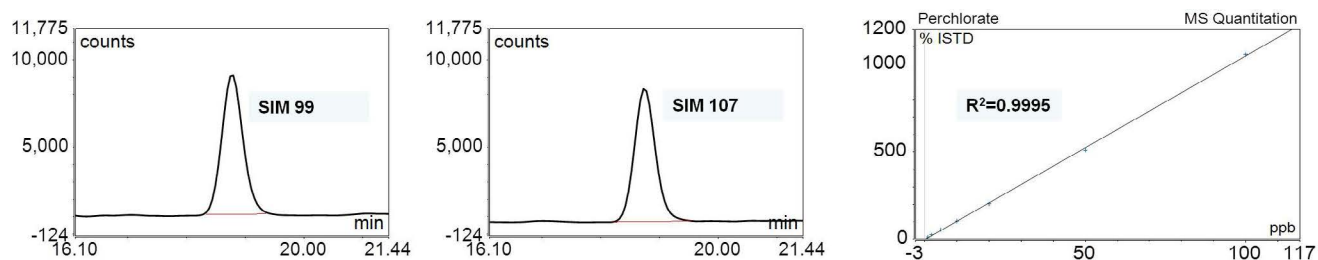
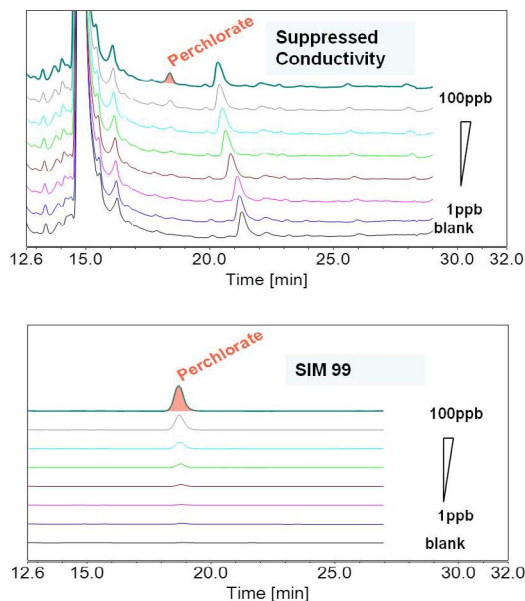


FIGURE 4. The benefits of mass detection.



Sample Preparation	ASE™-IC ¹	ASE™-IC-MS
Basic Alumina	✓	✓
OnGuard H (Hydronium)	✓
OnGuard Ag (Silver)	✓
OnGuard Ba (Barium)	✓
OnGuard RP	✓
24 Hour pre-incubation	✓
Preconcentration Column	✓
Sample Quantity	3 grams	1 gram

The selectivity of mass detection alleviates problematic separations using suppressed conductivity detection alone (Fig. 4). Fruit and vegetable matrices notoriously include high levels of background ions that interfere with resolution, detection, and quantitation particularly at low parts-per-billion concentrations. The strawberry matrix presented considerable challenges for chromatographic resolution of perchlorate, particularly due to high background conductance. Without mass detection, extensive sample preparation and clean-up procedures are required for reliable and accurate results (Fig. 4).

CONCLUSIONS

- In this method, sample prep, chromatography, and mass detection procedures are harmonized for a total workflow solution that leverages throughput, precision, and sensitivity.
- Adding mass detection eliminates cumbersome sample preparation steps needed for analyzing in complex fruit and vegetable matrices while also delivering enhanced performance.
- Overall, this method is adaptable and can be applied to other complex plant matrices or contaminants in which mass selectivity can enhance method performance and sample throughput.

REFERENCES

1. Richter, Bruce and Murphy, Brett. Determination of Perchlorate in Vegetation Samples Using Accelerated Solvent Extraction and Ion Chromatography. Application Note 356, 2005. Thermo Scientific.

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