

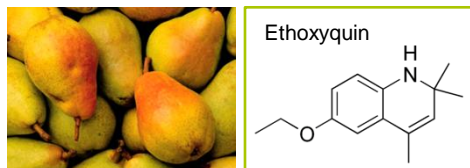
Impact of Ascorbic Acid in the Analysis of Ethoxyquin

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Introduction

Ethoxyquin is a quinoline-based antioxidant widely applied to inhibit superficial scald (formation of brown spots) on pears and apples. As scald is often accompanied by fungus infections, ethoxyquin is often listed as a fungicide. For treatment, fruits are typically dipped in a solution containing ethoxyquin. Ethoxyquin-impregnated fruit wraps are also employed.



Pre-harvest applications have also been reported for apples. Applying the QuEChERS method, ethoxyquin shows notoriously low recoveries for certain types of commodities such as pears, apples and cucumbers, but very good recoveries for other types of commodities exhibiting a strong antioxidative potential such as citrus fruit and berries (see Fig. 1). Ethoxyquin decomposes both in the crop as well as at various stages of the analytical procedure, including sample processing, extraction and storage of sample extracts. Interestingly, the degradation rates become slower following dSPE cleanup with PSA, indicating that PSA removes certain matrix components that promote the degradation of ethoxyquin.

Legal aspects

In 2011 it was decided not to include ethoxyquin in Annex I of Reg. 91/414/EEC, with a grace period ending in September 2012. EU-MRLs were set at the agreed LOQ of 0.05 mg kg⁻¹ for all commodities with the exception of pears, for which the MRL is 3 mg/kg⁻¹. Additional food-related uses of ethoxyquin include spices such as chili, paprika and curcuma powder. Here ethoxyquin is applied as an additive to prevent the oxidative discoloration of carotenoid pigments during storage.

Analytical method

To prevent oxidative losses and to increase ethoxyquin recoveries we employed the antioxidant ascorbic acid (AA) either just prior to milling (x g/100 g sample) or just prior to the QuEChERS extraction (1 mL of an aqueous solution containing 0.3 g/mL AA). Analysis was performed applying a QuEChERS extraction and measurement via LC-MS/MS (ESI-positive mode).

LC-Conditions:

Column: Acquity UPLC BEH C18 1.7µm, 2.1x100mm
Pre-Column: Acquity BEH C18, 2.1x5 mm, 1.7 µm
Mobile Phase:

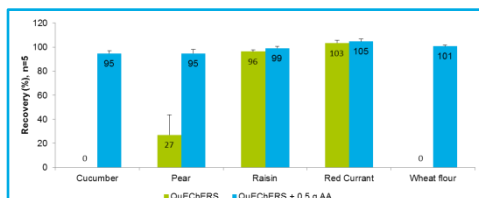
- A: 5 mMol NH₄-formiat 5 % MeOH in H₂O
- B: 5 mMol NH₄-formiat in MeOH

Method details: www.eurl-pesticides.eu

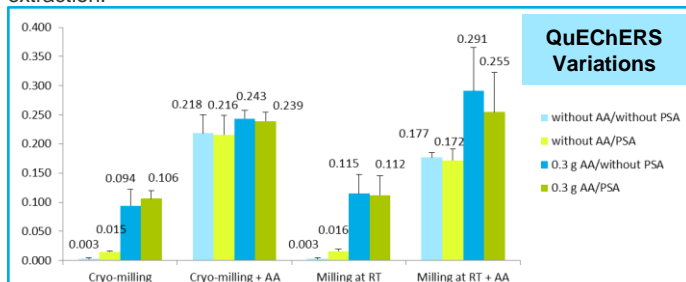


Results

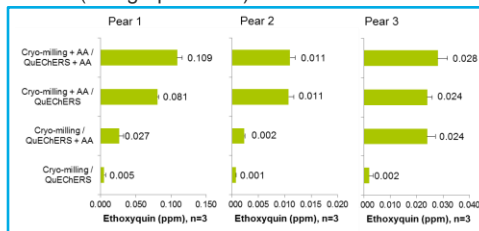
When spiking ethoxyquin with homogenates of commodities not exhibiting sufficient antioxidative protection (e.g. pears, see graph below) AA had to be added to the test portions as quickly as possible to minimize degradation.



Furthermore, we spiked fresh, whole pears with ethoxyquin and checked whether we could prevent ethoxyquin degradation by adding AA just prior to milling. The samples were partly milled cryogenically and partly comminuted at room temperature (see graph below). The addition of AA led to increased ethoxyquin yields. When milling pears at an ambient temperature the addition of AA prior to milling was also helpful, but the consumption of AA was so high that additional AA was necessary prior to QuEChERS extraction.



We repeated the experiment using market pear samples containing incurred ethoxyquin residues. The addition of AA resulted in a dramatic increase in the determined ethoxyquin levels here as well (see graph below).



Summary

When dealing with pears containing incurred residues the highest yields of ethoxyquin were obtained when AA was added to coarsely cut, frozen pieces prior to cryogenic milling. When milling pears at an ambient temperature the further addition of AA was necessary prior to QuEChERS extraction to minimize degradation.

Reference

1. www.eurl-pesticides.eu

