

## A novel analytical approach for the determination of ethylene-thiourea and propylene-thiourea in vegetal foodstuffs by HPLC-ICP-MS/MS

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Dithiocarbamates (DTC) are one of the most largely used fungicides in agriculture as they are cost-effective against a broad spectrum of fungi and plant diseases. DTC are highly instable and they tend to decompose in foodstuffs matrix into ethylene-thiourea (ETU) and propylene-thiourea (PTU). Currently, these contaminants are determined using organic-based mass spectrometry techniques (MS or MS/MS) coupled to high performance liquid chromatography (HPLC). Due to the sulphur (S) moiety in their structure, they can also be determined using inorganic based MS techniques such as inductively coupled plasma-triple quadrupole mass spectrometry (ICP-QQQMS or ICP-MS/MS) coupled to HPLC.

This study reports a novel approach allowing the simultaneous determination of ETU and PTU in fruits and vegetables by (reverse phase) HPLC coupled to ICP-MS/MS. A baseline HPLC separation of ETU and PTU was achieved in less than 5 min.

A robust method validation by using the accuracy profile approach was performed by carrying out four measurement series in duplicate at six different levels over a timespan of four weeks (different days). The spike recovery factors range from 87%-101% for ETU and from 98-99% for PTU (depending on the spiking level). Good coefficients of variation in terms of repeatability and intermediate-reproducibility were also obtained. The limit of quantification was 0.022 µg kg<sup>-1</sup> (wet weight) for ETU and 0.010 µg kg<sup>-1</sup> (ww) for PTU.

This approach was proved to be highly robust and suitable for the determination of ETU and PTU in foodstuffs of vegetal origin. In our knowledge, it is the first reported method in the literature to deal with the analysis of ETU and PTU from fruit and vegetable samples using ICP-MS based detection techniques. This novel approach opens also the possibility to apply species-specific isotope dilution, a primary method of analysis, for the determination of these organic contaminants.

**Keywords:** Ethylene-thiourea; Propylene-thiourea; HPLC-ICP-MS/MS; fruits; vegetables

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