

## SUMMARY

Citrus fruit production in Argentina is one of the activities of fundamental importance in the national and regional economy. It supplies the internal and the foreign market with fresh and processed fruits.

The use of agrochemicals during production in the field and packaging, for the control and treatment of diseases of citrus, involves residues in treated fruits. It is essential to monitor pesticide levels remaining in fruits, for both fresh consumption and for use as raw material in the processing industry. At present, citrus fruit exports have considerably increased. As a result, the demands on tolerance levels for pesticide residues have also been increasing, so is of special relevance the availability of analytical techniques able to assess levels of pesticides at trace levels.

The overall objective of this study was to establish the correlation between the initial levels of agrochemicals in oranges reaching the processing industry of essential oils and the levels found in the finished product (essential oils dewaxed). For this, another general objective was established that was to validate analytical methodologies to determine chlorpyrifos, carbendazim, prochloraz and thiabendazole by gas chromatography and liquid chromatography, coupled with mass spectrometry, in different citrus matrices (orange and orange essential oil dewaxing).

In whole fruit, the gas chromatography technique with mass spectrometric detector type simple quadrupole (GC-MS), was used for quantification of chlorpyrifos and prochloraz, while for carbendazim and thiabendazole quantification, liquid chromatography/tandem mass spectrometry detection (triple quadrupole) (LC-MS/MS) was used. For essential oils LC-MS/MS was used for determining prochloraz, carbendazim and thiabendazole, and gas chromatography/tandem mass spectrometry detection (triple quadrupole) (GC-MS/MS) for quantification of chlorpyrifos.

The extraction techniques employed were solvent extraction and dispersive solid phase extraction. To check the matrix effect, blank samples of oranges from organic production and essential oils made from them were used. For each method linearity, accuracy, precision, limit of detection and limit of quantification were assessed.

All methods evaluated were linear in the range of concentrations studied in the different matrices. The parameters of precision and accuracy in all cases showed values

within the range established for accurate and precise methods. The limits of detection and quantification obtained were adequate, taking into account the maximum residue limits (MRLs) established in Argentina and European legislation, for oranges.

The residues evaluated in orange samples, which reach the industry exhibited values below MRLs established in Argentina and the European Union. For all the pesticides evaluated, a correlation between the levels in the fruit and residual values obtained in essential oils, could be established.

The development and validation of analytical methods of these four pesticides, in oranges and essential oils dewaxed, can provide a valuable tool for the industrial sector, with which to determine accurately and precise levels of pesticides in the products they buy, produce and/or market. This will help to improve the quality control processes, allowing the operator to select only raw materials that meet the criteria required by the legislation on residues, as well as to establish appropriate marketing strategies, taking into account the differences in MRLs that exist in the different markets.

**Keywords:**

Citrus, Essential oils, Pesticides, Validation, Gas chromatography, Liquid chromatography.