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# Endogenous generation of $CS_2$ during dithiocarbamate residue analysis in *Carica papaya L*

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The main problem associated to dithiocarbamate residue analyses is the phytogenic $CS_2$ generation. This fact is well known for some plant species in which the $CS_2$ background levels may reach the established Maximum Residue Limits. The endogenous $CS_2$ formation, as well as other volatile sulfur compounds like carbonyl sulfide, may be related to the degradation of natural isothiocyanates, which are derived, by their turn, from an enzymatic degradation of different glucosinolates present in dicotyledonous plants. In the *Caricaceae* family the benzylglucozinolate is founded in all parts of the plant as well as the benzylisothiocyanate and methylthiocyanate. The purpose of this work was to investigate, under the conditions of dithiocarbamate residue analysis, the endogenous formation and the background level of $CS_2$ in *Carica papaya L.*, cultivars *Golden* and *Sunrise Solo*, grown without any treatment with sulfur agrochemicals, either pesticide or fertilizer.

The seedlings of papayas were obtained of seeds without chemical treatment and papayas were cultivated in two representative Brazilian production areas. Fruits were harvested at 0, 1 and 2 ripening stages, being the two later stages those of the commercial harvesting practice. Samples of whole papaya fruits, crushed and uncrushed, and fractionated into pulp, peel and seeds were submitted to the experimental conditions of dithiocarbamate residue analysis using the isooctane partitioning (de Kok, 2000) and headspace procedures. The $CS_2$ was quantified by GC/FPD operating in the sulfur mode and the $CS_2$ presence in papaya extracts was confirmed by GC/ITD – EI technique. At least six replicates of each papaya fraction were analyzed.

The $CS_2$ was observed in almost all of the analyzed samples. There was an increase of $CS_2$ levels corresponding to the increase of ripening stages (from 0 until 2). No significant differences were observed between the cultivars *Golden* and *Sunrise Solo.*

The highest $CS_2$ levels were in seeds and peels which varied from <0.03 to 0.18 mg $kg^{-1}$ (isooctane) and 0.06 to 0.57 mg $kg^{-1}$(headspace). In pulp the $CS_2$ was not detected or was <0.03 mg $kg^{-1}$. Crushed whole fruit samples always gave higher results than the uncrushed fruit, however with no statistical meaning. These results follow the same pattern of occurrence of benzylisothiocyanates in papaya, which are higher in peels and seeds and increase with the ripening stages.

These $CS_2$ levels might be higher in papaya cultivated in presence of sulfur fertilizers.

Dithiocarbamate MRL's established at the analytical method sensitivity should be reviewed for cultures with phytogenic $CS_2$ generation. These $CS_2$ backgrounds have induced erroneous conclusions about dithiocarbamates residues in papaya inside the European Union, causing the refusal of Brazilian papaya exports.

## Reference

de Kok A & Van Bodegraven P., (2000). EPRW 2000 3rd European Pesticide Residue Workshop, Book of Abstracts, p. 170. York: UK