

Comparison on the Effect of different Light Sources on the Fate of 1,2,3,6-tetrahydro-*N*-(trichloromethylthio) phthalimide Using LCMS

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ABSTRACT

The photodegradation of 1,2,3,6-tetrahydro-*N*-(trichloromethylthio) phthalimide [captan -(CPT)] on apple surfaces by different UV radiation (UV-C -254 nm and full UV spectra – 250 – 750 nm) was investigated. Results obtained demonstrate the UV – light irradiance on apple surfaces has the capability of markedly reducing the concentration of surface sorbed levels of CPT (which is frequently detected on fruit surfaces) through direct and possibly indirect photochemical degradation. The loss of CPT was found to be significant for the experimental conditions described here, with >80% loss of initial concentrations of the test chemical under UV-B & C light within 30 minutes of light exposure. In general, CPT decayed more quickly under the UV A-B compared to UV –C. The rate of degradation (k_{CPT}) was found to be 2.0×10^{-3} and $3.1 \times 10^{-3} \text{ min}^{-1}$ for the Xenon “750 W/m^2 ” and UV-C lamps respectively with corresponding half-lives of 346.5 min and 22.57 min. Photolysis of CPT is usually as a result of the homolytic dissociation of a C-Cl bond.

Keywords: UV-B, photodegradation, pesticides, Solar UV simulator, UV-C

1.0. Introduction

Pesticides have been in use since the 1940s and have found increased use mainly in the agricultural sector for the controlling of pests (Ukpebor et al. 2011, Grung et al. 2015). The use of pesticides is an integral part of the world’s food production as shown by the fact that more than 2.5 million tons of these anthropogenic chemicals were applied to soil and foliage in 1996 alone (Bachman and Patterson 1999). However, their toxicity on both target and non- target organisms is quite worrisome. Some of these pesticides have been found to cause alterations to DNA/RNA regions of MCF – 7 mammalian cells at environmentally relevant concentrations (Ukpebor et al. 2011). More so when they have become one of the most frequently occurring pollutant in nature (Tajeddine et al. 2010).

Captan (1,2,3,6-tetrahydro-*N*-(trichloromethylthio) phthalimide) is used to control fungal disease on a wide variety of crops and seeds in Canada. It also has a broader industrial application for control of mould in paints, lacquers and wallpaper pastes. CPT acts through inhibition of a fungal process of respiration and metabolism through a non-specific thiol reactant (Barreda et al. 2006, Rawn et al. 2008). CPT was detected in fruit and vegetables during market basket monitoring and total diet studies (Rawn et al. 2004, USA FDA 2006, Sadlo et al. 2007). It is the most frequently detected fungicide in some market basket studies and average concentrations were reported to be relatively high (98 ng/g) (Krol et al. 2000). CPT is used extensively to control diseases such as grey mould fungus (*Botrytis cinerea*), which is found in both pre-harvest and post-harvest strawberries (Ritcey et al. 1987, Blacharski et al. 2001). CPT residue levels in other fruit and vegetables also have been measured (Frank et al. 1983, Fernandez-Cruz et al. 2006, Rawn et al. 2007). Research has determined CPT dissipation rates, levels in fruit and absorption rates by field workers (Ritcey et al. 1987, Krieger and Dinoff 2000), however there is no work on the fate on apple surfaces to the knowledge of the author.

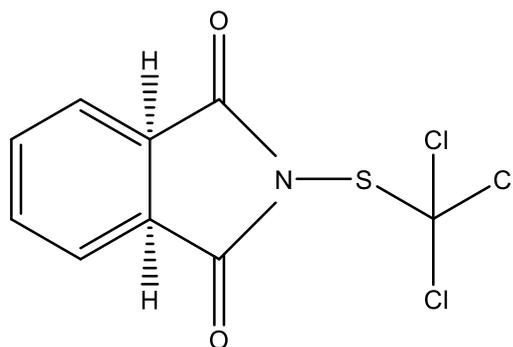


Figure 1: Chemical structure of captan (1,2,3,6-tetrahydro-*N*-(trichloromethylthio) phthalimide) IUPAC - (3*aR*,7*aS*)-2-[(trichloromethyl)sulfanyl]-3*a*,4,7,7*a*-tetrahydro-1*H*-isoindole-1,3(2*H*)-dione, mol. wt. = 300.59 g/mol

Considering the potential human and wild life health risks associated with toxic pesticides, it is necessary to under their behaviour once released into the environment and assess conditions that may accelerate or inhibit their longevity. This work was therefore designed to study the effect of the different light sources on the photochemical degradation of CPT on apple surfaces.

2.0. Materials and methods

2.1. Chemicals

Captan analytical grade standard was purchased from Sigma Aldrich (Poole, UK). High purity solvents (methanol and acetonitrile), suitable for LC and residue analysis, were purchased from Fisher Scientific (UK).

2.2. Apples preparation

The apples were sorted into preparation group according to size and were then stored at 4 °C. Selected apples were held under running de-ionized water for 10–15 s with continuous rubbing by hand. Following preparation, apples were cut in half with a clean knife, apple slices was placed in glass vials. 10 µL of 10 mg/L CPT solution was pipetted unto the apple surface and allowed to evaporate. The apple samples were then irradiated under the different light sources to investigate photodegradation. Samples were also placed in the dark to act as control. Triplicate experiments were conducted.

2.3. Extraction and sample preparation

Extraction at the end of the irradiation time was carried out but adding ~10 mL of methanol into the vessels and sonicated for about 30 seconds. The internal standard – methyl parathion was then added to 1 mL of the methanol extract for analysis on the LCMS.

2.4. Photodegradation experiments

Photodegradation was carried out in an Atlas Suntest CPS+ solar simulator (Atlas, Germany) (Figure 2) fitted with the Xenon arc lamp without a UV-filter and under a UV-C lamp ($\lambda = 254\text{nm}$). After an initial warming period, the lamp provided a consistent light output with the internal temperature of the light-chamber maintained using Thermoquest water bath (ThermoFinnigan UK) at 20°C (± 2.0). 200 mL glass vessels (60 x 75 cm) were used for both experiments. 10 µL CPT solutions was applied uniformly across the apple surface using a micropipette (0.05 and 0.1 mg per apple for CAP). The solution was allowed to evaporate from the apple surface at room temperature before being transferred to the base of one of the reaction vessels. Treated apples were also placed in the dark to serve as controls and account for pesticide loss due to other processes such as volatilisation.



Figure 2: Atlas Suntest CPS+ light chamber equipped with a Xenon arc lamp set at the maximum irradiance setting of 750 W/m²

2.5. Instrumental conditions

All analyses were performed using a Thermo Deca Liquid Chromatography – Mass Spectrophotometer (LCMS) equipped with a Thermo Surveyor Autosampler and Photodiode Array detector (PDA). This was interfaced with an Ion – trap MS

2.6. Quality assurance/quality control

Additional apples with no spiking was also prepared in the same manner. The blank and spiked apples were extracted alongside each other.

A previously developed pesticide application method was employed for introducing the actives on the surface of the apples (Ukpebor 2011). Untreated samples were also included in the sample pool; CPT was not detected in the untreated samples. The rate of degradation of the active ingredients CPT is presented in Figure 3, which illustrate degradation on the apple surfaces exposed to light under both the Xenon and UV-C lamps. Significant decay of both actives was observed in all experiments and found to follow first order kinetics (Eq. 1). This demonstrated reduced CAP and CPF longevity on irradiated apple surfaces compared to control samples (i.e. pesticide-coated apples stored in the dark). Rate of pesticide loss was derived from the first-order rate expression:

$$\ln (C_t/C_0) = -kt \quad (1)$$

where C_t is the concentration (mg or mmol) of the actives on the apple surface after a certain light-exposure time, C_0 is the initial concentration on the apple surface (mg or mmol), and t is time (in mins) and k is the degradation rate (min^{-1}). Use of equation (1) allows the derivation of the pesticide half-life ($t_{1/2}$) on the apple surface, where $t_{1/2} = k/0.693$.

3.0. Results and Discussion

3.1. Captan

The rate of degradation of CPT on the apple surfaces was significant for both experimental setups. The rate of degradation (k_{CPT}) was found to be 2.0×10^{-3} and $3.1 \times 10^{-3} \text{ min}^{-1}$ for the Xenon “750 W/m²” and UV-C lamps respectively. These rates were found to have corresponding half-lives of 346.5 min and 22.57 min. Figure 2 shows the degradation profile of CPT under the Xenon and UV-C lamps.

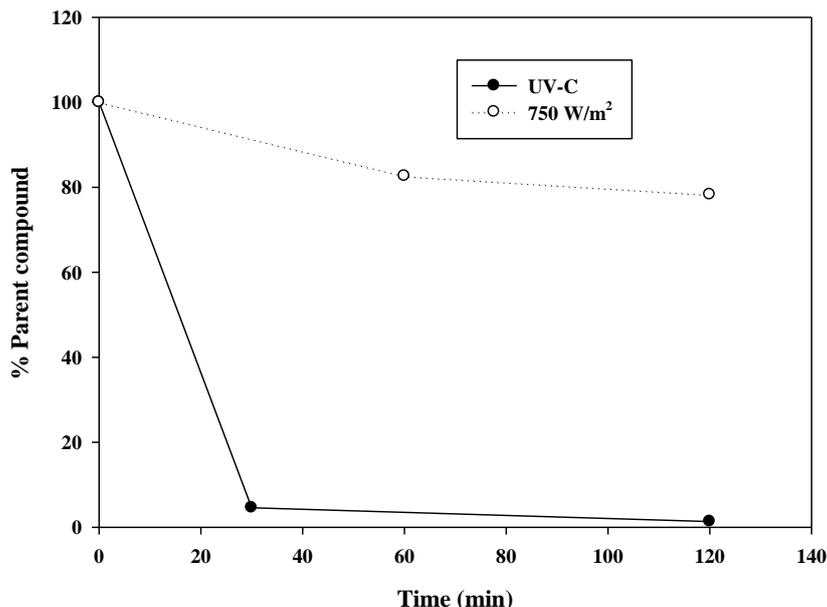


Figure 3: Photodegradation of CAP on ‘organic jazz’ apples under the UV-C and Xenon

Pesticide degradation was found to be significant in all light-exposure experiments (relative to control apples kept in the dark) and ranged from ~20-80% degradation of the initial quantity applied to the apple surfaces. CPT applied at a nominal concentration of 50 μg (or 0.05 mg) and 100 μg (or 0.1 mg) respectively per apple degraded under both the Xenon and UV-C lamp exposures. Use of the UV-C lamp increased the rate of CAP decay ($t_{1/2} = 22.6$ mins) by a factor of ~ 16 relative to the Xenon lamp set at 750 W/m^2 ($t_{1/2} = 346.5$ mins). This is attributable to the absorption spectrum of CAP where maximum light absorption for this chemical occurs within the UV-C region (100 – 280 nm) (see Figure 4). CAP possesses maximum light absorption (λ_{max}) at 180 nm, and the impact of its absorption profile on its degradation is evident in the rates of degradation and half-lives. Examination of Figure 3 reveals notable degradation in the first 30 mins of exposure under the UV-C lamp (~80% loss), suggesting a rapid non-first-order decay, followed by a possible slowing of the degradation rate after 30 mins exposure. Comparing the longevity of CPT under the various lamps showed that k_{CPT} for the xenon lamp lower than k_{CPT} for the UV-C lamp. Clearly, these results indicate that UV light (notably UV-C) will degrade pesticide residues on fruit surfaces (certainly for the common ‘active’ studied here).

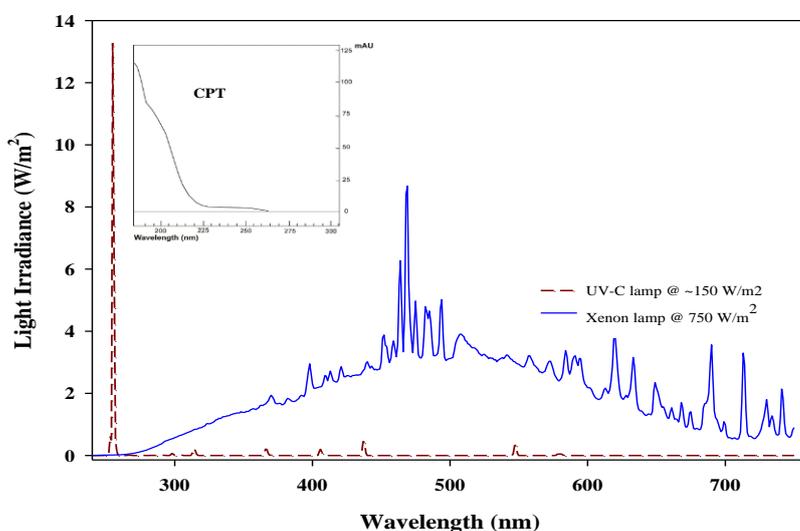


Figure 4: Spectral irradiance (I) of the UV-C lamp (brown dashed line) and xenon lamp (blue line). Inset: Absorption spectra of CPT in acetonitrile/water (80/20 V/V)

Comparison of the results here to similar work was not possible as there was no prior research to the knowledge of the author to compare the findings with.

4.0. Conclusion

For most of the experimental apples the initial quantity of pesticide applied to the surface of the apple resulted in a concentration which was less than the maximum residue level (MRL) for the respective pesticide, highlighting the realistic nature of the experiments with regards to the quantity of pesticide under investigation. Both captan and chlorpyrifos absorb light in the UV-B/C regions of the light spectrum accounting for their degradation most notably under the UV-C light source. The benchmark for chemical loss being >80% degradation of the initial surface-sorbed quantity. Future work would also examine degradation on 'wet' apple surfaces to further improve/promote pesticide degradation under UV light.

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