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1 **Determination of Chlorpropham (CIPC) residues, in the concrete flooring of potato**
2 **stores, using quantitative (HPLC UV/VIS) and qualitative (GCMS) methods.**

3

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10

11

12 **Highlights**

13

14 CIPC is lost to the concrete fabric of potato stores during application.

15

16 HPLC UV/VIS method developed and validated to detect CIPC in concrete.

17

18 CIPC presence in concrete confirmed by GCMS.

19

20 CIPC is persistent in the concrete flooring of potato stores at 4 cm depth.

21

22 Top 1 cm of flooring contains > 90 % CIPC.

23

24 **Abstract**

25 Isopropyl-N-(3-chlorophenyl) carbamate (CIPC, common name Chlorpropham) is commonly
26 used for post-harvest sprout inhibition in stored potatoes. It is applied as a thermal fog which
27 results in loss to the fabric of the store and the atmosphere. Recently, there have been
28 concerns in the United Kingdom because of cross contamination of other crop commodities
29 that were stored in buildings with a history of CIPC usage. This cross contamination may
30 have occurred because of retained residues in the fabric of the stores. The retention of CIPC
31 in concrete is poorly understood; therefore the requirement for a robust analytical method for
32 the detection and quantification of CIPC in concrete is a critical first step in tackling this
33 problem. A method using High-Performance Liquid Chromatography with ultraviolet
34 detection (HPLC UV/VIS) was validated. CIPC recoveries at three concentration levels (0.4,
35 4.0 and 40.0 $\mu\text{g g}^{-1}$) were in the range of 90.7-97.0 % with relative standard deviations
36 between 2.14-3.01 %. The limits of detection and quantification were 0.03 and 0.1 $\mu\text{g g}^{-1}$,
37 respectively. This study confirmed that CIPC was persistent in concrete to a depth of 4 cm,
38 with > 90 % within the top 1 cm of the flooring.

39

40 **Keywords**

41 Chlorpropham, Concrete, Potato Stores, HPLC UV/VIS, GCMS.

42 **1. Introduction**

43 Potato (*Solanum tuberosum L.*), with an annual production of 375 million tons (Flis *et al.*,
44 2014), is globally the fourth largest staple crop after rice, wheat and maize (Wang *et al.*,
45 2011). The potato is an essential part of the diet for more than a billion people worldwide
46 (Cicatelli *et al.*, 2014) and is a staple food in temperate regions of the world, while in other
47 parts of the world it is generally used as a vegetable (Kibar, 2012).

48 China produces nearly 60 million tonnes, followed by India, Russia and the USA (Food
49 Innovation Online Corp, 2017). The total production in the United Kingdom (UK) for the
50 2015 crop year was 5.49 million tonnes (AHDB-Potatoes). Potato tubers can remain suitable
51 for consumption or processing through long periods of storage after harvest. They are
52 considered one of the most important foods worldwide because of their long storage life
53 which enables the potato processing industry to operate year-round in locations where
54 potatoes can only be produced during a favourable growing season. After harvest, potato
55 tubers are dormant for several weeks but continue to be metabolically active. However, as the
56 tubers progress through the physiological aging process, from the dormant to the non-
57 dormant phase, they become able to produce sprouts which have the potential to grow into a
58 new plant (Daniels-Lake *et al.*, 2013).

59 Sprouting of stored potatoes results in weight loss and a decrease in nutritive value
60 (Hajššlová and Davídek, 1986). Sprouting also increases glycoalkaloid production during
61 storage (Friedman and Levin, 2016) which in turn causes a bitter taste (Maga and Fitzpatrick,
62 1980). Sprouting can be minimised, to maintain their long-term quality, by the use of
63 chemical sprout inhibitors. The most common and effective in the potato industry is
64 Isopropyl-N-(3-chlorophenyl) carbamate (CIPC, common name Chlorpropham, Figure 1)
65 (Frazier and Olsen, 2014). CIPC is typically applied as a hot fog on harvested potatoes which
66 causes deposition of solid residues on the potatoes (Gouseti *et al.*, 2015). Prior to the CIPC

67 Stewardship Group recommendations which implemented lower CIPC application rates
68 (PICSG, 2016), the greatest total dose of CIPC that could be applied to potatoes in the UK
69 was 63.75 g per tonne (McGowan *et al.*, 2009). Recent research conducted using application
70 rates of 12-14 g per tonne for potatoes for the fresh market (held at a storage temperature of
71 3-4°C), and 23-26 g per tonne for potatoes for processing (held at a storage temperature of 7-
72 9°C), has shown that 23 - 25 % and 5 - 10% of input CIPC, respectively, was retained as a
73 residue on tubers after storage (Briddon *et al.*, 2014). Non-target fates of CIPC have been
74 detailed by Smith *et al.* (2013) and include losses to the environment, including the
75 atmosphere, soil, waterways and the fabric of the store.

76 The persistence of CIPC in soil and aquatic environments has been extensively studied. The
77 half-lives of CIPC in soil at temperatures of 15 °C and 29 °C were 163 and 27 days,
78 respectively, whereas in lake water, the half-life was 2208 days (Smith and Bucher, 2012).
79 On the contrary, the persistence of CIPC in the fabric of stores is poorly understood and this
80 has recently become of concern in the UK because of cross contamination of other crop
81 commodities that were stored in buildings with a history of CIPC usage. This is particularly
82 problematic as the presence of detectable amounts of CIPC in any commodity, except ware
83 potatoes, renders it unfit for use in the EU. This also applies to manufactured food products,
84 with the exception of potato products. For instance, cross contaminated wheat that was used
85 in the production of baby rusks (Farley Brand Heinz) resulted in thousands of packets of the
86 product being withdrawn from UK shops after they were found to be contaminated with
87 CIPC (Curtis, 2006).

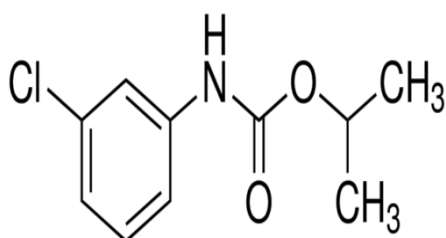
88 The problem of cross contamination of other crop commodities by CIPC can be attributed in
89 part to the changing commercial pressures within agriculture and also advancement in
90 instrumental analysis. Many of the medium to small size potato producers, in particular, are
91 moving away from the potato sector and wish to utilise the vacated stores for other purposes.

92 This has always caused problems, even for those farmers remaining in the potato sector, who
93 also grow cereals, due to the fact that seed crops of any type coming in contact with a CIPC
94 contaminated store, even for a short period of time, may have impairment of germination and
95 blanking. Chemical residues in crops are a serious trade barrier (Randhawa *et al.*, 2014) and
96 the utilisation of storage facilities previously treated with CIPC for any commodity is
97 problematic in terms of cross contamination and may lead to an exceedance of the Maximum
98 Residue Level (MRL). In the European Union, MRLs are established at the limit of
99 quantification if a pesticide is not authorised for use on a specific crop (EFSA, 2011). In the
100 UK, crops such as cereals, onions and oilseeds do not have approval for CIPC use and
101 therefore they have an MRL at the limit of quantification (limit of determination) which is
102 0.01 mg kg⁻¹ (EFSA, 2011; personal communication T Cowl, CRD-HSE 20 April 2017). As
103 the detection limits for pesticides continue to improve due to advancements in instrumental
104 analysis, crops can now be analysed and deemed to be contaminated at levels that in the past
105 would have been below the limit of detection.

106 The residual quantities of CIPC lost to the fabric of the store are important, particularly if the
107 store will be used for housing other crops. Over the years, various analytical methods have
108 been employed to detect CIPC in soil (Clark and Wright 1970; Alsehli, 2014), water (Guzik,
109 1978; Park *et al.*, 2009; Passananti *et al.*, 2014; Alsehli, 2014), air (Boyd and Duncan, 1986
110 a; Boyd and Duncan, 1986 b; Park, 2004), on stored potatoes (Camire *et al.*, 1995; Khan *et*
111 *al.*, 2012; Mohammed 2012; Mohammed 2015) and in bacterial metabolism (Clark and
112 Wright, 1970; Vega *et al.*, 1984). However, studies on CIPC analysis in building materials
113 are almost completely lacking. Boyd and Duncan (1986b) reported on the accumulation of
114 CIPC residues in the concrete structures of a potato store and demonstrated concentrations in
115 the concrete walls and flooring in the range of 130-290 mg kg⁻¹ and 2050-9470 mg kg⁻¹,
116 respectively. However, this method involved time-consuming Soxhlet extraction followed by

117 a flame ionisation detection (GC-FID) method which is less sensitive for CIPC compared to
118 other methods such as HPLC UV/VIS (Mohammed, 2014). Therefore, alternative, higher
119 sensitivity analytical methods are required to detect CIPC in building materials, to allow
120 informed recommendations to be made to farmers about the re-use of stores for other crop
121 commodities.

122 The objectives of this present study were to develop a simple and robust method for detecting
123 CIPC in concrete and to use this method to investigate the concentration of CIPC and the
124 spatial and depth distributions in the concrete flooring of a contaminated store.



125
126
127
128 Figure 1. The chemical structure of Isopropyl-N-(3-chlorophenyl) carbamate (CIPC, common
129 name chlorpropham).

130

131 2. Materials and Methods

132 2.1 Material

133 Isopropyl N-(3-chloro-phenyl) carbamate (CIPC, 98 % purity) was obtained from Sigma-
134 Aldrich (Dorset, United Kingdom). HPLC-grade solvents (acetone and acetonitrile) were
135 purchased from Fisher Scientific (Loughborough, United Kingdom). Ultrapure water was
136 obtained using a Millipore Elix[®] 5 water purification system (Molsheim, France). HPLC
137 grade vials with PTFE screw caps (Agilent technologies, USA), syringe filters (13 mm) with
138 0.2 μm PTFE membrane (VWR International, USA), luer lock syringes (3 ml) (HSW

139 NORM-JECT[®] Germany) and 20 ml glass vials (PerkinElmer, USA) were obtained from
140 Crawford Scientific Ltd, UK.

141 A reconstituted stone slab of dimensions 100 × 200 × 50 mm (Bradstone UK), containing a
142 mixture of stone and cement, was chosen to represent the concrete content of the store floor.

143

144 2.2 Preparation of CIPC stock solution

145 A stock solution of CIPC was prepared in acetonitrile at a concentration of 1000 µg mL⁻¹.
146 Calibration standard solutions (0.01-1.0 µg mL⁻¹) and spiking solutions were prepared by
147 diluting the 1000 µg mL⁻¹ stock with acetonitrile as required.

148

149 2.3 Sample preparation

150 2.3.1. Preparation of blank concrete matrix for method development.

151 Concrete blocks (Brandstone, UK) were chopped into approximately 25 g portions using a
152 hammer and chisel. These were then crushed using a Retsch[®] Jaw Crusher (Haan, Germany),
153 collected in a 125 µm Endecotts sieve (London, England) and shaken at 175 r.p.m for 30
154 minutes on a Retsch[®] Shaker (Haan, Germany). Sieved samples (≤125 µm), representing the
155 blank concrete matrix, were stored in 20 ml screw cap glass vials at room temperature.
156 Recovery experiments were performed using 5 g portions of blank concrete matrix, spiked
157 with CIPC stock solutions of 100 µg mL⁻¹ and 1000 µg mL⁻¹ to give concentrations of 0.4,
158 4.0 and 40 µg g⁻¹ CIPC to concrete content. A 30 minute period was allowed for the CIPC to
159 interact with the concrete matrix and for evaporation of solvent. Five replicates were prepared
160 for each spiking level. Extracted concrete samples of 40 µg g⁻¹ CIPC to concrete content were
161 diluted 1:10 with acetonitrile (100 %) prior to analysis.

162 2.3.2. Coring of concrete flooring in a potato store and preparation of industrial concrete
163 cores for analysis.

164 The floor was cored using a Titan drill and a 52 mm diamond-tipped corer. A pilot drill bit (8
165 mm diameter) was used to enable the corer to grip the concrete surface. The pilot drill bit
166 penetrated the concrete to a depth of 0.5 cm and was subsequently removed from the drill.
167 This prevented contamination of the lower layers during the coring process. The coring was
168 continued with the diamond tipped corer and extracted cores were wiped free of dust. A new
169 pilot drill was used for each core and the corer was cleaned with methanol between samples.
170 It was postulated that CIPC may penetrate the concrete to a depth of 3 cm, therefore, a 7 cm
171 core was initially collected to assess the depth of penetration and the risk of contamination
172 during the drilling and processing of samples. The intact 7 cm core was weighed prior to
173 sectioning (using a Lapidary trim saw (Mukilteo, USA) into 1 cm layers, from the bottom to
174 the top to prevent CIPC residues from transferring to the lower layers. The layers were
175 crushed and prepared, as previously described, in ascending order from bottom to top. Two
176 other cores were collected from the same store and the length of each core, and hence the
177 number of layers from each, depended on the ease of penetration of the drill into the concrete.
178 These cores were processed in the same manner as the 7 cm core. A section of clean concrete
179 block, which was used in the method development, was routinely crushed and analysed in
180 between contaminated industrial core samples to ensure the robustness of the processing
181 method.

182

183 2.4. Extraction procedure.

184 After the 30 minute interaction period for recovery experiments, acetonitrile (20 mL) was
185 added to the respective 5 g samples of spiked blank concrete matrix. The samples were

186 placed on an orbital shaker (IKA) set at 20°C for 30 minutes at 175 r.p.m and then left at
187 room temperature overnight. The following morning, the samples were shaken for a further
188 15 minutes at 20°C and 175 r.p.m. A glass Pasteur pipette was used to transfer the
189 supernatant from each container into 20 mL glass vials. For each sample, a 2 mL disposable
190 syringe was used to remove approximately 1 mL of the supernatant which was filtered
191 through a 0.2 µm PTFE membrane syringe filter into a 2 mL HPLC vial and the extract
192 stored at 4 °C for analysis. Finally, 20 µL of the extract was analysed by high-performance
193 liquid chromatography with UV detection (HPLC UV/VIS) and gas chromatography mass
194 spectrometry (GCMS). The extraction procedure for the processed industrial concrete
195 samples was the same as for the recovery experiments, with the exception of the weight of
196 concrete extracted. One gram of crushed industrial concrete of particle size 125 µm, from
197 each layer of a core, was separately extracted in 20 mL acetonitrile. Extracted industrial
198 concrete samples were diluted to a concentration range of 0.01 to 1.0 µg mL⁻¹ prior to
199 analysis.

200 2.5. Instrumentation and operation conditions.

201 2.5.1 HPLC UV/VIS

202 The analysis of the CIPC residues in concrete was carried out using a High-Performance
203 Liquid Chromatography system (Shimadzu, Kyoto, Japan) with a Rheodyne® injector model
204 7725, an isocratic pump (LC-20 AD Prominence Liquid Chromatograph Shimadzu), a DGU-
205 20 A₃ Prominence Degasser (Shimadzu) and a SPD-20 A Prominence UV/VIS Detector
206 (Shimadzu). Data acquisition and processing were performed with LC Solution software
207 release 3.40.

208 The chromatographic separation was performed at 25°C on a Genesis analytical column (250
209 mm × 10 mm i.d. 4 µm). The mobile phase was acetonitrile and ultrapure water in a ratio

210 60:40 (v/v) which was delivered at a flow rate of 1.5 mL min⁻¹. The UV chromatographs
211 were recorded at 210 nm. The identification of CIPC in concrete samples was achieved by
212 comparing the retention times with those of standard CIPC solutions. Residual CIPC was
213 flushed from the injector between analyses using 3 mL of acetonitrile. The column was
214 washed with acetonitrile for 10 or 20 minutes between analyses, then an acetonitrile blank
215 was analysed between analyses to ensure that there was no carryover.

216

217 2.5.2. GCMS

218 A Shimadzu GC MS-QP 2010 instrument was used for analysis. Separations were carried out
219 using a ZB-5MS column (30 m x 0.25 mm i.d. 0.25 µm film thickness) with a stationary
220 phase comprising 5% Phenyl-Arylene and 95% Dimethylpolysiloxane (Phenomenex®, UK).
221 The temperatures of the injector and detector were set at 220 °C and 260 °C, respectively. The
222 injection volume was 1 µL at a purge flow of 3 mL min⁻¹ in splitless mode. Total run time for
223 analysis was 19.20 minutes with an initial temperature of 80 °C and hold time of 0.5 minutes,
224 followed by a four step temperature increase: i) + 30 °C min⁻¹ to 125 °C for one minute, ii) +
225 25 °C min⁻¹ to 180 °C for 3 minutes, iii) + 25 °C min⁻¹ to 280 °C for 4 minutes, iv) + 20 °C
226 min⁻¹ to 300 °C for 2 minutes. The carrier gas was helium which was maintained at a constant
227 pressure of 10.3 psi with a linear velocity of 38.1 cm sec⁻¹ at 80.0 °C (oven temperature).
228 Parameters for the MS were as follows: electron impact (EI) source temperature of 260 °C,
229 interface temperature of 250 °C. Ion masses were scanned from 40 to 350 m/z at 3333 scans
230 per second. Data acquisition and processing were performed with LabSolution software,
231 GCMS Solution version 2.50 SU1. The identification of CIPC in concrete samples was
232 achieved by comparing the mass spectral patterns with those of standard CIPC solutions and
233 by using NIST/EPA/NIH mass spectral library (NIST 05) and NIST mass spectral search
234 program version 2.0d.

235

236 3. Results and discussion

237 3.1. Method validation for HPLC UV/VIS

238 The only relevant HPLC UV/VIS method previously developed is for CIPC in potato extracts
239 by Khan *et al.* (2008, unpublished) and discussed in detail in Mohammed (2012). The method
240 developed here is for concrete and is validated for accuracy, precision and linearity. Prior to
241 the development of the method for concrete, the instrument response for CIPC was assessed
242 and the method was validated using CIPC standard solutions. The precision of the standard
243 solutions was determined using 10 replicate injections of 1 $\mu\text{g mL}^{-1}$ CIPC solution with high
244 precision obtained for the standard solutions (Relative Standard Deviation (RSD) % = 1.59).
245 Linearity was assessed (in triplicate) using standard calibration curves that were constructed
246 by plotting the signal intensity versus the concentration of CIPC in the standard solutions.
247 Excellent linearity was obtained in the concentration range from 0.01 to 1.0 $\mu\text{g mL}^{-1}$, with
248 correlation coefficients (R^2) greater than 0.99. Extracted industrial concrete samples were
249 diluted to fit this concentration range prior to analysis (Figure 2). Sensitivity was evaluated
250 by estimating the limit of quantification (LOQ) and limit of detection (LOD) using a repeat
251 injection method (n=10) (Mohammed *et al.*, 2014). The LOD and LOQ values, with respect
252 to the instrument response to CIPC, were evaluated using 0.01 $\mu\text{g mL}^{-1}$ CIPC solutions. The
253 LOD and LOQ values of 0.001 $\mu\text{g mL}^{-1}$ and 0.004 $\mu\text{g mL}^{-1}$ were equal to 3 and 10 times the
254 standard deviation (SD) of the 0.01 $\mu\text{g mL}^{-1}$ CIPC solution, respectively. The LOD and LOQ
255 values, with respect to the extraction procedure, were evaluated using spiked (nominal level
256 0.04 $\mu\text{g g}^{-1}$; n=10) and non-spiked (n=10) concrete samples. The SD was calculated using a
257 repeat injection method for both spiked (n=10) and non-spiked (n=10) samples, as depicted in
258 the following equation: $SD = \sqrt{[(SD_s)^2 + (SD_b)^2]}$ where spiked and non-spiked concrete are

259 designated SD_s and SD_b , respectively. The LOD and LOQ values of $0.03 \mu\text{g g}^{-1}$ and $0.1 \mu\text{g g}^{-1}$
 260 were equal to 3 and 10 times the SD of the spiked and non-spiked concrete matrix extracts
 261 respectively (Mohammed, 2012). The accuracy and precision of the method with respect to
 262 concrete was determined by recovery tests ($n=5$) conducted at three concentration levels,
 263 using the blank concrete matrix spiked at concentration levels of 0.4, 4.0 and $40 \mu\text{g g}^{-1}$. The
 264 extraction procedure was highly efficient with recoveries greater than 90%. The precision
 265 was assessed by calculating the %RSD of the five determinants per concentration (Table 1).

266 Table 1. Quantitative determination of CIPC in spiked reconstituted concrete ($n=5$) using
 267 HPLC UV/VIS at 210 nm.

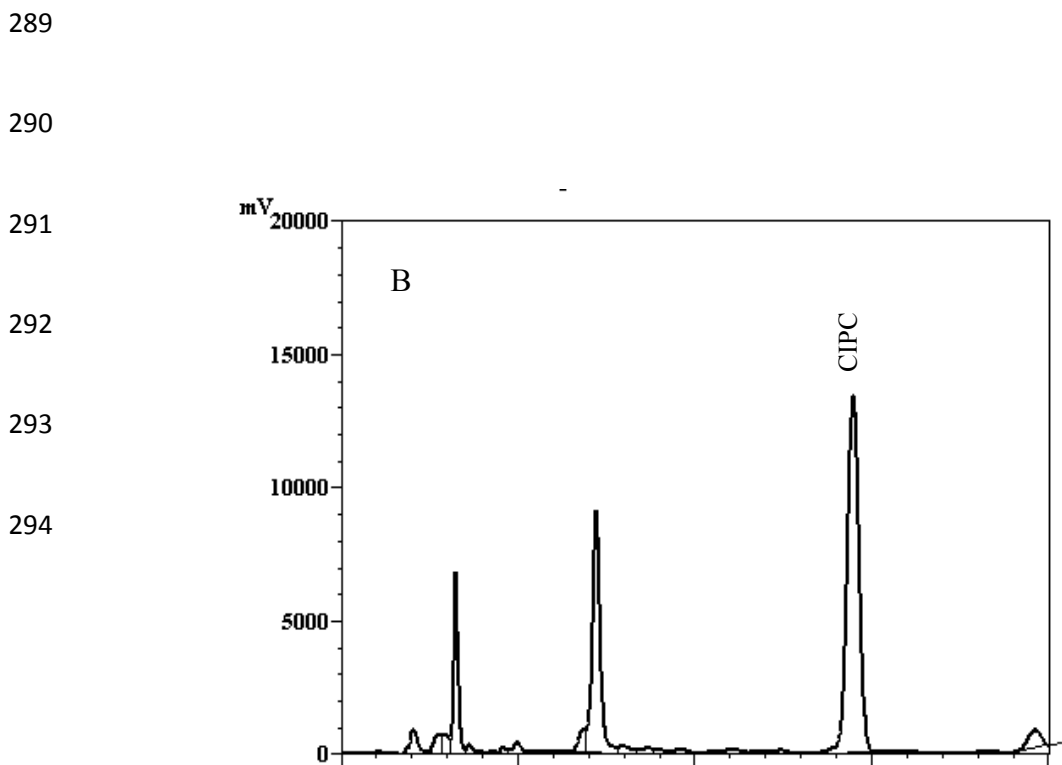
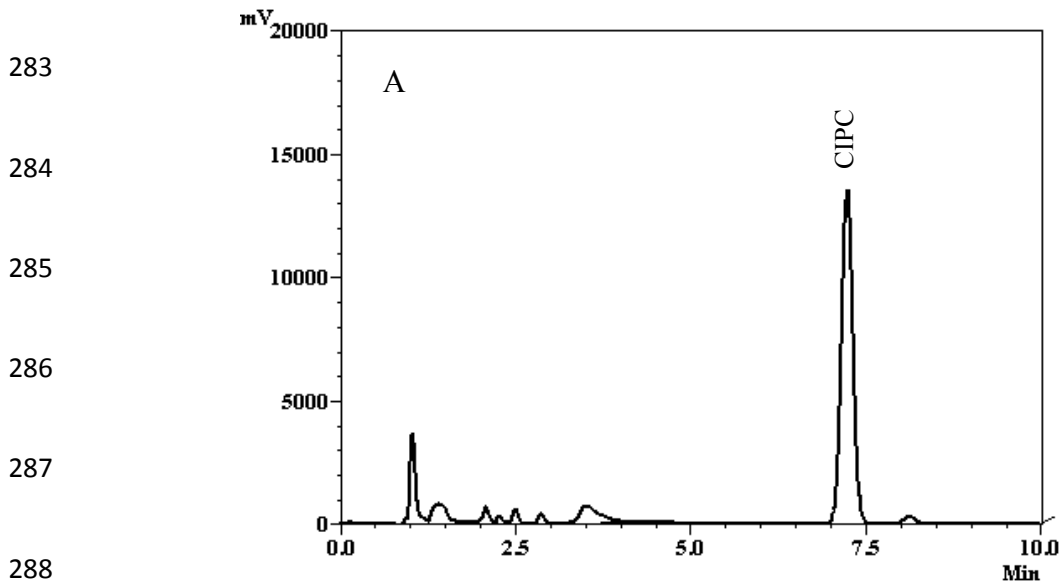
268

Nominal concentration in extract ($\mu\text{g g}^{-1}$)	Mean concentration recovered from concrete ($\mu\text{g g}^{-1}$)	Recovery % (\pm % RSD)	LOD ($\mu\text{g g}^{-1}$)	LOQ ($\mu\text{g g}^{-1}$)
0.4	0.388	97.0 ± 3.01	0.03	0.1
4.0	3.747	93.7 ± 2.43		
40.0	36.275	90.7 ± 2.14		

269

270 The HPLC UV/VIS method was developed using an isocratic system with manual injection.
 271 Although reproducible data were generated using this system, there were limitations in terms
 272 of the time required for manual washing of the injector and column which became more
 273 apparent when ‘real’ concrete samples were analysed. For the purpose of high throughput

274 analysis, the following recommendations are made. A binary system with automated injection
275 would allow a programme with a gradient step and an injector rinse step to be included. This
276 would remove residual CIPC from the column and injector respectively, thus ensuring no
277 carry over between analyses. The concrete contents of the blocks used in the method
278 development can be considered as modern concrete. The method was initially used to assess
279 the CIPC concentrations in a research potato store and was efficient in terms of CIPC
280 quantification. The concrete content and structural integrity of concrete in other commercial
281 stores may be different from the concrete contents of the blocks used in the method
282 development therefore, further assessment and development may be required.



295

296

297

298 Figure 2. HPLC UV/VIS chromatograms at retention time 7.2 minutes for: (A) A CIPC
299 standard solution of $1.0 \mu\text{g mL}^{-1}$ and (B) an industrial concrete sample contaminated with
300 CIPC.

301

302 3.2 Depth distribution of CIPC into the concrete flooring of a research potato store.

303 The depth of CIPC distribution into the concrete flooring of the research potato store was
304 determined by sectioning concrete cores, obtained from designated positions in the floor of
305 the store, into one centimetre depth increments. Each increment from the respective cores
306 was processed, extracted and the resulting industrial concrete samples analysed by HPLC
307 UV/VIS. The depth of CIPC distribution was expressed as μg of CIPC per gram of concrete
308 in each layer. The majority of CIPC (between 90 and 100 %) was found in the top
309 centimetre layer of each core, with a decrease in concentration in the subsequent layers. CIPC
310 penetrated the concrete flooring of the store to a depth between 3 and 4 cm. The
311 concentrations in layers 1-7 of the 7 cm core were 23, 1.5, 0.31, 0.22, 0.0, 0.0 and $0.0 \mu\text{g g}^{-1}$,
312 respectively. The absence of CIPC in the last three layers demonstrates that there was no
313 contamination during the drilling process. The levels in the second core were 266 and $1.2 \mu\text{g}$
314 g^{-1} for the top and second layer respectively; whereas for the third core, the values were 179,
315 0.53 and $0.26 \mu\text{g g}^{-1}$ for the top, second and third layer, respectively.

316

317 3.3 Qualitative analysis of CIPC in spiked and industrial concrete using GCMS.

318 A GCMS method to confirm the presence of CIPC in industrial concrete samples and the
319 spiked blank concrete matrix was also developed. Both spiked and industrial concrete
320 samples gave mass spectral patterns which were consistent with the expected spectrum
321 obtained from the NIST database:

322 (<http://webbook.nist.gov/cgi/cbook.cgi?Name=chlorpropham&Units=SI&cMS=on#Mass-Spec>)

323 (213/215 m/z: parent ion; 153/154 m/z: m-chlorophenyl isocyanate; 171/173 m/z: free acid
324 formed from isopropyl residue; 127/129 m/z: chloraniline) (Figure 3).

325

326 3.4 The risks of cross contamination of crops stored in the vicinity of contaminated concrete
327 flooring.

328 In this study, a research store with 23 years of CIPC applications was assessed for CIPC
329 presence and levels in the concrete flooring. This store was routinely steam cleaned after the
330 applications, however, the levels detected in the cores demonstrate that CIPC is persistent,
331 even after extensive cleaning. This highlights the possible risks of cross contamination of
332 crops in this research store and potentially, even higher risks in commercial stores which do
333 not employ cleaning strategies. The issue of cross contamination is currently of concern in
334 the UK, and crop assurance schemes such as Red Tractor recommend risk assessments to
335 ensure that crops can be safely stored without becoming cross contaminated. A preliminary
336 risk assessment method is proposed here, employing the data derived for 2 cores using the
337 methods outlined above. These data are ideal for determining the concentrations and presence
338 of CIPC in concrete and will provide useful input data for developing calculations involving
339 risk assessments. For example, using the total CIPC concentration in the 7-cm deep core
340 ($25.03 \mu\text{g g}^{-1}$), a risk assessment can be calculated using the density of concrete ($2,400 \text{ kg m}^{-3}$)

341 or 2.4 g cm⁻³). The amount of CIPC present in 1 m² of the concrete flooring will be 601.4 mg
342 m⁻² [0.07 x 2400 x average CIPC concentration (25.03 / 7) mg]. Assuming that wheat is
343 stored to a depth of 5 m, that the average density of wheat is 720 kg m⁻³ and that an estimated
344 20% of the CIPC migrates into the wheat in any one season, then the average concentration in
345 the wheat would be 0.03 mg kg⁻¹. The permissible limit of CIPC in crops other than potatoes
346 is 0.01 mg kg⁻¹, therefore we can conclude that the average concentration in the wheat is a
347 factor of x3 higher than the limit, however, the 20% loss per season from concrete is likely to
348 be a significant overestimation, given that we have detected CIPC up to a depth of 4 cm in a
349 store where 25 years had elapsed since the last application (Douglas et al., unpublished).
350 Similarly, if we take the 2-cm depth core, which has a total of 267.2 µg g⁻¹, and using the
351 same parameters as above, this would equate to 0.36 mg kg⁻¹ in the wheat, 36x the limit.

352 The ease of volatilization of a chemical is related to its vapour pressure and the rate of
353 movement from the volatilizing surface (Smith and Bucher, 2012), therefore, it may be
354 feasible for CIPC to volatilize from the concrete surface into the headspace of the store.
355 Tomlin (2003) quotes a vapour pressure value for CIPC of 24 mP at 20 °C while Taylor and
356 Spencer (1990) quote 1.3 mP at 25 °C. However, there is no information pertaining to the
357 volatilization of CIPC from concrete. Current research is being conducted to investigate the
358 rate of volatilization from a concrete surface and the route of cross contamination of crop
359 commodities in stores with a history of CIPC usage. This will provide invaluable information
360 for improved risk assessments and decontamination strategies, including the application of
361 sealants to the concrete flooring to prevent CIPC volatilization.

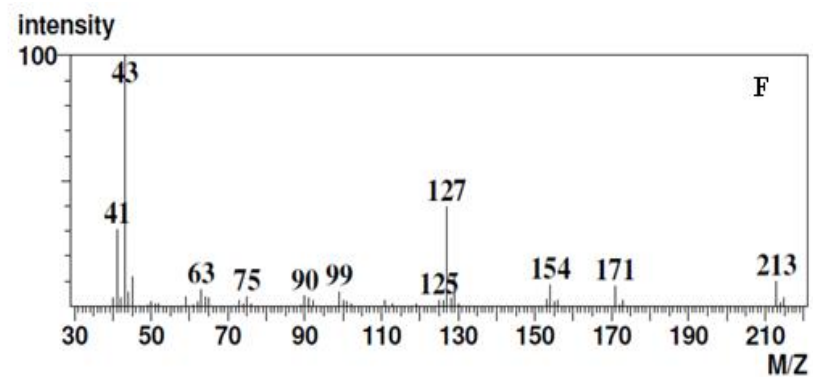
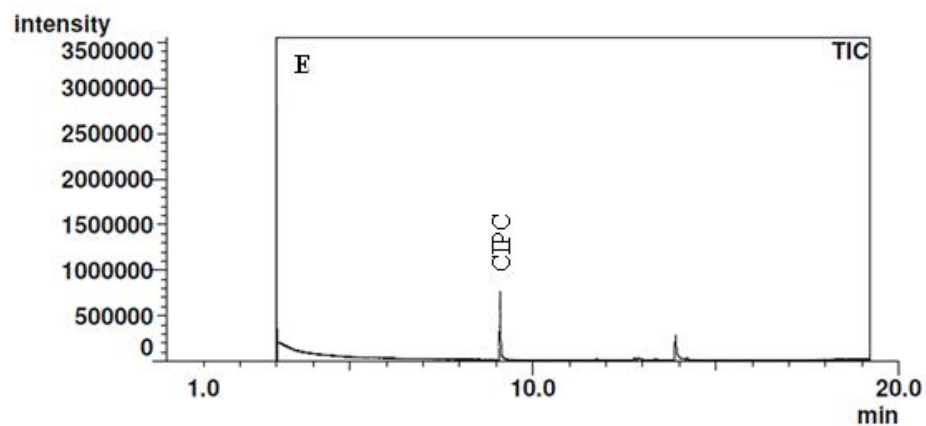
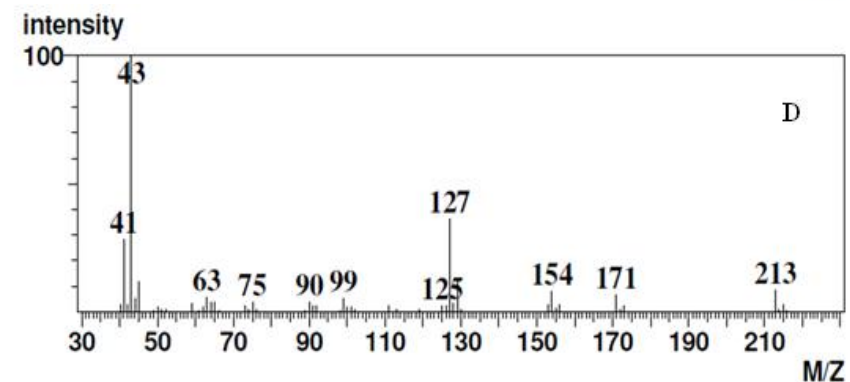
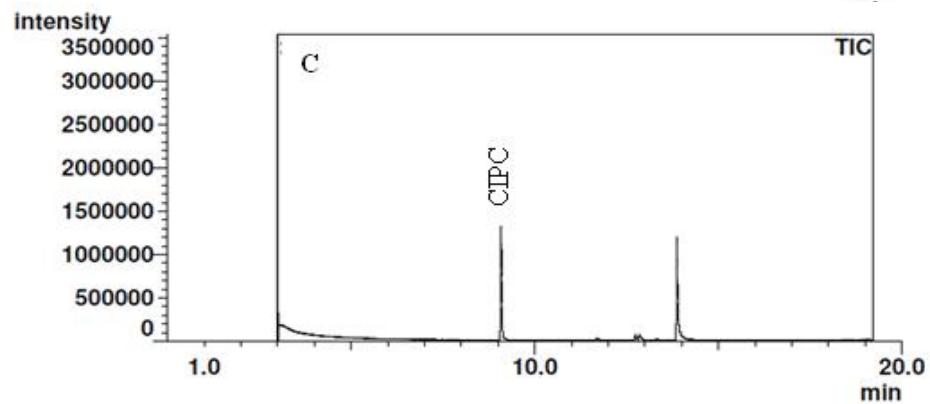
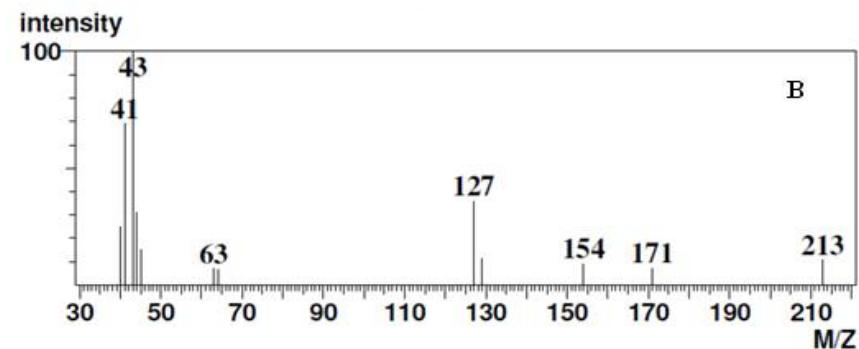
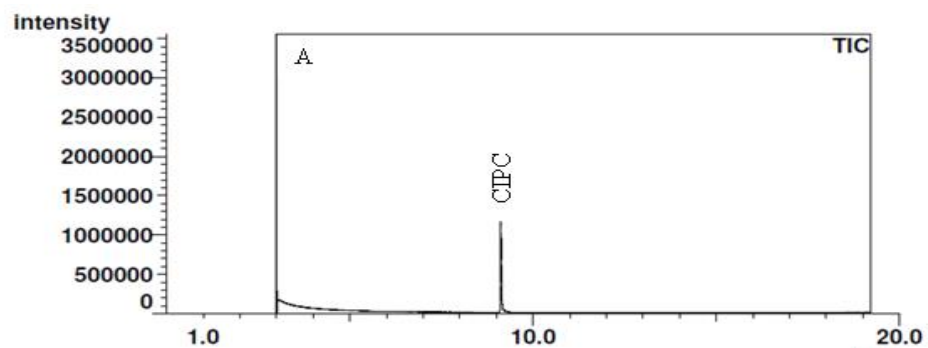


Figure 3. GCMS chromatograms and mass spectra obtained at a retention time of 9.1 minutes for a CIPC standard solution of $10.0 \mu\text{g mL}^{-1}$ (A & B), a spiked concrete sample at $40 \mu\text{g g}^{-1}$ CIPC to concrete content (C & D) and an industrial concrete sample contaminated with CIPC (E & F).

362 **4. Conclusion.**

363 A simple, reproducible and more sensitive analytical method for determining residues of
364 chlorpropham (CIPC) in concrete, using HPLC UV/VIS, was developed and validated.
365 Acceptable recoveries of $\geq 90\%$ were obtained with high precision (% RSD 2.14-3.01).
366 Triplicate analyses from a representative industrial concrete sample suggested that the
367 accuracy, precision and selectivity of the proposed method were satisfactory for CIPC
368 detection in the concrete of commercial potato stores. The limits of detection and
369 quantification were 0.03 and 0.10 $\mu\text{g g}^{-1}$, respectively, allowing application of the method for
370 very low residue levels. The presence of CIPC in the concrete flooring was confirmed by
371 GCMS. An assessment of CIPC distribution in the flooring showed that it can persist to a
372 depth of 4 cm. This highlights the risk of possible cross contamination of other crop
373 commodities stored in potato stores with a history of CIPC usage. A preliminary risk
374 assessment calculation, using an actual CIPC level in the concrete flooring of a research store
375 (266 $\mu\text{g g}^{-1}$ in the top 1-cm), suggests the potential risk of cross contamination of grain (0.36
376 mg kg^{-1}), exceeding the permissible limit.

377

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