A Simplified Method for Determining Sprout-Inhibiting Levels of Chlorpropham (CIPC) in Potatoes

A simplified method for determining sprout-inhibiting levels of chlorpropham in aerosol-treated potatoes (*Solanum tuberosum* L.) has been developed. The method involves a petroleum ether extraction and subsequent quantification via flame ionization gas–liquid chromatography. The method is sensitive to parts per million and gives excellent recovery with good precision.

Isopropyl *m*-chlorocarbanilate (CIPC) is routinely used to inhibit sprouting of potatoes in storage. A separate study, involving the change in CIPC concentration in commercial storages, emphasized the need for a simple, yet sufficiently precise, method for determining residue levels on large numbers of tuber samples. Previously used methods included gas–liquid chromatography (GLC) (Sator and Patzold, 1974; Van Vliet and Hertog, 1966; Fishbein and Zelinski, 1965; Gutenmann and Lisk, 1964), infrared spectroscopy (Ferguson et al., 1963), and colorimetry (Bleidner et al., 1954; Montgomery and Freed, 1959; Ferguson and Gard, 1969). For sample preparation all of these methods require either lengthy extraction steps or varying degrees of cleanup, often both. Most GLC methods, although very sensitive, also require the formation of a derivative, a step that is both time consuming and contributes to inaccuracy.

Using the colorimetric procedure of Ferguson and Gard (1969), it was found that the levels needed for sprout inhibition were considerably above 1 ppm in the peel layer (Corsini et al., 1976). Sator and Patzold (1974) found that most of the aerosol-applied CIPC residue in white potatoes is within the peel layer which includes the periderm and cortical region. It does not appear to be necessary, therefore, to use whole tubers for sprout inhibition studies as CIPC residues are then diluted tenfold, requiring more sensitivity for accurate results. Consequently, the following method for measuring peel residue levels above the 1 ppm level was developed. This method is suitable for large-scale monitoring of stored potatoes for changes in CIPC concentration following aerosol treatment.

MATERIALS AND METHODS

CIPC, 99.1% purity, was supplied by Chemical Division, PPG Industries, Inc., Barberton, Ohio. All solvents were reagent grade.

All GLC separations were performed in a Hewlett Packard 5830A gas chromatograph with flame ionization detector and glass columns (1200 × 2 mm) containing 3% w/w OV-1 on 100/120 mesh Gas-Chrom Q. The column was previously conditioned for 24 h at 250 °C.

The method of Ferguson and Gard (1969) was modified to eliminate the digestion and first distillation steps and was then used for comparison with the GLC method. Frozen potato peel was ground to a uniform consistency with a hand mortar and pestle using liquid nitrogen to maintain the peel in a frozen state until transferred to a 33 × 94 mm Soxhlet extraction thimble. Continuous extraction with dichloromethane gave maximum recovery after 20 h. The dichloromethane extract was evaporated at 35 °C under minimum vacuum and the residue hydrolyzed in 100 mL of 50% (w/v) NaOH as described by Ferguson and Gard (1969).

Sample Preparation. The sample consisted of eight sound tubers, 170–280 g. The tubers were not washed, but all loose dirt was brushed off with paper toweling. Tuber peel was completely removed to a uniform depth using a kitchen hand peeler. Peel thickness was approximately 2 mm. The peel sample was thoroughly mixed, immediately quick frozen with liquid nitrogen and stored below −10 °C.

Extraction. A sample of approximately 35 g was removed and ground with a mortar and pestle to a uniform size while in the frozen state, using liquid nitrogen. A 25-g subsample was weighed into a 500-mL Erlenmeyer flask, 200 mL of petroleum ether was immediately added, and the flask was covered with aluminum foil. The sample was allowed to sit 20 h at room temperature with occasional swirling. The petroleum ether extract was carefully decanted without filtration into a 500-mL evaporation flask. The residue was washed twice with 50-mL portions of extracting solvent. The solvent was evaporated to near dryness at 35 °C under minimum vacuum using a rotary film evaporator. Using higher temperatures or allowing the residue to remain at this temperature or under vacuum for any length of time will result in considerable losses of the somewhat volatile CIPC. Five milliliters of *n*-hexane was added to the sample in the evaporation flask and agitated until solution was complete. The concentrated extract was transferred to a small vial, sealed, and stored under refrigeration until ready for GLC analysis. There was no change in GLC response to CIPC levels in solutions stored in this way for up to 3 weeks.

GLC Procedure. Injections were made directly into a single column as described above under the following conditions: helium carrier flow, 42 mL/min, hydrogen 55 mL/min, air 250 mL/min; injector temperature, 200 °C, detector 275 °C. The oven temperature was held at 100 °C for 5 min, then increased to 200 °C at a rate of 10 °C/min, held 1 min, then cooled. Each analysis cycle took 20 min. Peak areas were determined with the aid of a Hewlett Packard 18850A GC terminal.

Unknown sample concentrations were estimated through the use of external standards run daily. Response was linear with a slope of 1.00 in the range of 1–2 μg injected.

Confirmation of CIPC peaks in unknown samples was made by adding a known amount of CIPC to the final extract solution just before injection.

RESULTS AND DISCUSSION

The modified colorimetric procedure of Ferguson and Gard (1969) gave 84 ± 22% recovery of added CIPC in the range of 1–25 ppm in a series of 20 recovery tests. A set of unknown samples collected from storages treated with aerosol-applied CIPC was run cooperatively at our facility and at Barberton Laboratories of PPG Industries, Inc. Our values corrected for average recovery were 103 ± 16% of the Barberton values determined by infrared spectroscopy (Ferguson et al., 1963). The colorimetric method was our standard in developing the GLC procedure. Although the colorimetric procedure was sufficiently sensitive, an improvement in precision was hoped for. The colorimetric procedure was also labor intensive, requiring much laboratory space and specialized glassware limiting the

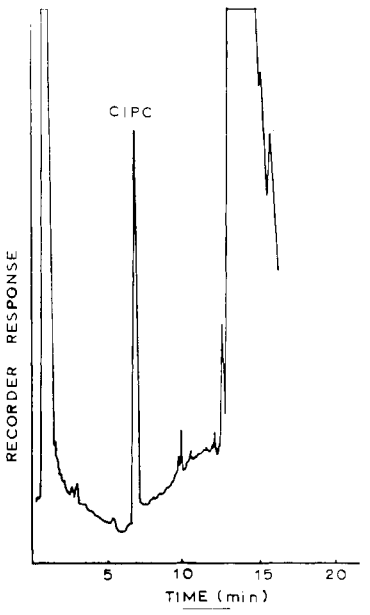

Figure 1. GC chromatogram of petroleum ether extract of potato peel containing 14 ppm CIPC.

number of samples that could be run on a day-in, day-out basis. This was a definite disadvantage in a method which was to be applied to the routine monitoring of CIPC levels in many large potato storages.

Preliminary tests using the colorimetric procedure described above indicated that sprout-inhibiting levels of CIPC in the peel were approximately 20 ppm and that the flame ionization detector gave sufficient sensitivity for the range of sample concentrations from 1 to 500 ppm.

The relative volatility of CIPC was combined with the low retention and high stability of OV-1 to give very consistent GLC separations over many weeks of daily use. The 20-min analysis time per sample was somewhat long, but the simple extraction procedure with no cleanup compensated for this. The crude extract after concentration was analyzed directly. CIPC elutes as a sharp peak in about 6 min (Figure 1). After CIPC measurement, contaminants were eluted by increasing the column temperature; the temperature-stable OV-1 could be "cleaned" occasionally by leaving overnight at 250 °C. No problems were experienced with buildup of contaminants on the column. No interference from other pesticides or naturally occurring materials extracted by petroleum ether has been noted in several hundred samples. The potatoes analyzed were grown and stored under a variety of conditions and represented a considerable range of cultural treatments that might be expected to cause test interference.

The lower limit of quantitative determination under these conditions was 1 ppm or 25 μg/standard 25-g peel sample. This was slightly less than the sensitivity of the colorimetric procedures. Other GLC procedures (Gutenmann and Lisk, 1964; Van Vliet and Hertog, 1966) are more sensitive, but are also more time consuming.

Table I. Recovery of CIPC from Fortified Samples of Potato Peel Analyzed by the GLC Procedure

Amount added,[a] μg	Actual ppm	Amount recov. μg	Estimated ppm	% recov.
400	16	390	16	98
400	16	460	18	115
800	32	730	29	91
800	32	807	32	101
1000	40	970	39	97
1200	48	1200	48	100
1600	64	1870	75	117
2000	80	1910	76	96

[a] CIPC solution in dichloromethane added directly to ground frozen peel sample in flask and mixed before addition of extracting solvent.

Recovery and precision using this method was superior to the colorimetric procedure and more samples could be analyzed with less chance of error. The results of a typical set of recovery tests using the GLC procedure are reported in Table I. The recovery from 35 fortification tests was 103 ± 14%. The average deviation from the mean in a series of replicate analyses using 33 unknown samples was 4 ppm or 15%. The analysis of a large number of unknown samples by both the colorimetric procedure and GLC procedure has given substantial confirmation of the increased efficiency of the GLC procedure.

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