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Large Volume Cold On-Column Injection for Gas Chromatography−Negative Chemical Ionization−Mass Spectrometry Analysis of Selected Pesticides in Air Samples

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A new gas chromatographic method is described for the analysis of fungicides captan, captafol, and folpet from organic extracts of air samples using large volume injection (LVI) via a cold on-column (COC) inlet coupled with gas chromatography−negative chemical ionization−mass spectrometry (GC-NCI-MS). Although standard split/splitless injection due to high injection port temperatures (>225 °C) have been shown to degrade these thermally labile fungicides, COC injection minimizes degradation. Insecticides such as chlorpyrifos and diazinon were also examined to show added selectivity. By using a solvent vapor exit with the COC inlet, injection volumes of 10−100 μL can be made to lower detection levels. GC-NCI-MS was compared to GC−electron impact ionization−mass spectrometry for each pesticide using LVI-COC injections and was found to be 2−80 times more sensitive, depending on the pesticide. Method detection limit (MDL) values with 100 μL injections were 2.5 μg L^{-1} for captan, folpet, and diazinon, 5.0 μg L^{-1} captafol, and 1.0 μg L^{-1} for chlorpyrifos, with the normal working range examined for sample analysis from MDL to 100 μg L^{-1}. Detection of all pesticides except captafol, used only in the United States but not Canada, was demonstrated from air samples taken from Abbotsford, British Columbia, Canada.

KEYWORDS: Cold on-column; large volume injection; gas chromatography−mass spectrometry; pesticides; fungicides

INTRODUCTION

Gas chromatography−mass spectrometry (GC-MS) has been used for the routine analysis of semivolatile pesticides in environmental, food, and vegetation samples. For most GC and GC-MS applications, split/splitless injection is the most frequent way of sample introduction (*1*). Some semivolatile analytes are prone to degradation in a split/splitless inlet due to the high temperature (>225 °C). Many multiresidue GC methods involve small splitless injection volumes (1−2 μL) at a heated temperature, typically 225−250 °C (*2*−*11*), where there is potential for degradation of thermally unstable pesticides. Degradation of N-trihalomethylthio fungicides can occur at elevated temperatures from sample preparation or storage or from GC analysis (*11*, *12*). Although there are many studies that use different selection of liners, such as double tapered deactivated glass, empty, or carbofrit liners, to thermally protect or reduce the residence times of captan and folpet in the injection port, degradation can still occur (*12*−*17*).

Cold on-column (COC) and programmable temperature vaporizer (PTV) inlets have been used to minimize degradation of thermally labile compounds during GC analysis (*12*, *16*−*23*). The PTV inlet for pesticide analysis using captan and folpet typically has an initial injector temperature ranging from 60 to 70 °C for ∼0.3−0.5 min, followed by a rapid temperature increase (e.g., 100 °C min^{-1}) to the desired maximum temperature of 280−330 °C (*12*, *16*−*23*). The PTV inlet can be used for small volume injections of 1−2 μL (*22*, *23*) but is commonly chosen to allow larger volume injections of up to 10 μL of sample (*12*, *16*−*20*, *22*). However, for thermally labile compounds, the rapid temperature increase in the inlet can still cause degradation (*12*). The COC inlet greatly reduces the risk of thermal degradation by directly injecting the sample cold (e.g., 60−70 °C) onto the GC column. One method has shown that COC injection resulted in increased sensitivity over PTV and pulsed splitless injections for the analysis of this class of

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thermally labile fungicides (*12*), although PTV is still the best approach for dirty matrix samples (*1*, *12*).

In addition to analyte degradation, the analysis is often limited for environmental samples as compared to food and vegetation samples by the detection limits and interferences in detection when electron impact ionization mass spectrometric (EI-MS) detection or electron capture detection (ECD) is used. Quantitative (qualitative) ions for selective ion monitoring (SIM) with EI-MS methods in food products, fruits, and vegetation are for captan [*m*/*z* 79 (264, 299)], captafol [*m*/*z* 79 (347, 349, 80)], and folpet [*m*/*z* 147 (104, 260, 295)] (*2*−*6*, *9*, *16*, *21*, *23*) with detection levels >100 μg L^{-1}. In addition, some of the qualifier ions for captan and captafol such as *m*/*z* of 264, 299, 347, and 349 are too low in abundance to be detected at the concentrations levels <1000 μg L^{-1}. In environmental samples (e.g., air sample extracts), the lower masses (<100−200) used for the quantitative ion often have interferences from other matrix or sample components even after sample cleanup. Multiresidue EI-MS/MS methods have also been utilized in food and vegetation analysis to provide greater confirmation and include multiple reaction monitoring (MRM) methods [parent (daughter ion)] for captan *m*/*z* of 263 (107, 148) (*14*) or *m*/*z* of 114 (79) (*2*) and folpet *m*/*z* of 260 (232) (*19*). Methods with chemical ionization have received little attention to date.

Captan and folpet are of particular interest in our studies due to their known use as fungicides in agriculture in the Lower Fraser Valley of British Columbia, Canada, on berry, fruit (e.g., apples), and vegetable crops. The Agriculture Canada/Environment Canada/Greater Vancouver Regional District (GVRD) (AQ Station T034) field monitoring station located in Abbotsford is in the middle of the Lower Fraser Valley in an area with extensive berry crops. No pesticide usage information is available for the study period of 2004−2005, but 2003 usages of captan, diazinon, and chlopryrifos in British Columbia were 25500, 27074, and 4561 kg, respectively (*24*). Captan and diazinon were in the top 20 pesticides used in 2003 in British Columbia. Although no usage information is available for folpet in the 2003 inventory, its use is suspected to be significant on berry crops with applications similar to that of captan (*25*).

In this paper, a new method to analyze the fungicides, captan, captafol, and folpet, which commonly exhibit degradation with splitless injection, is described, where large volume injection (LVI) using a COC inlet with solvent vapor exit (COC-SVE) and GC−negative chemical ionization−mass spectrometry (GC-NCI-MS) to minimize sample degradation and improve detection. Our goal is to determine the presence of trace levels of these fungicides below the 100 pg/m^3 range in weekly air samples, which was not possible using a standard splitless injection. For comparison, two organophosphorus pesticides (diazinon and chlorpyrifos) that do not exhibit thermal degradation in the injector port and are often measured in air samples at low to high levels in Canada are also provided to illustrate that the method is also applicable to thermally stable compounds when lower detection limits are required or interferences are present with EI-MS. Typically, chlorpyrifos levels at Abbotsford are too low to quantify levels without a LVI method. These analyses are the first to detect these fungicides in air samples in this agricultural region of Canada where there is known or suspected usage of pesticides such as diazinon, chlorpyrifos, captan, and folpet. Captafol, a N-trihalomethylthio fungicide used in the United States, has potential for long-range atmospheric transport to this region of Canada and consequently was included in the analytical method.

Table 1. Compound and *m*/*z* Ratios Employed in Identification and Quantification (Bold) with LVI-COC GC-NCI-MS

pesticide	NCI (*m*/*z*)	EI (*m*/*z*)	retention time (min)
captan	**150**, 151	**79**, 107, 149	13.92
folpet	**146**, 148	**260**, 262, 104	14.10
captafol	**150**, 151	**79**, 149, 264	18.04
diazinon	**169**	**304**,179,137	10.11
chlorpyrifos	**313**,315	**197**,199,270	11.69
diazinon (diethyl-d_{10})	**179**	**314**	10.05
parathion (diethyl-d_{10}) (internal standard)	**301**, 303	**301**, 303	11.87

MATERIALS AND METHODS

Materials. All standards were purchased from Chem Service Inc. (West Chester, PA). The pesticide standards included captan (N-[trichloromethylthio]-4-cyclohexene-1,2-dicarboximide, CAS RN 133-06-02, 100 μg mL^{-1} in toluene), captafol (N-[1,1,2,2-tetrachloroethylthiol]-4-cyclohexene-1,2-dicarboximide, CAS RN 2425-06-1, 100 μg mL^{-1} in toluene), chlorpyrifos (O,O-diethyl-O[3,5,6-trichloro-2-pyridyl]phosphorothioate, CAS RN 2921-88-2, 100 μg mL^{-1} in iso-octane), diazinon (O,O-diethyl-O-[2-isopropyl-4-methyl-6-pyridimyl]phosphorothioate, 100 μg mL^{-1} in toluene), and solid folpet (N-[trichloromethylthio]-phthalimide, CAS RN 133-07-3). Deuterated internal standard, parathion diethyl-d_{10} [O,O-diethyl-O-*p*-nitrophenyl phosphorothioate (diethyl-d_{10})], and surrogate, diazinon (diethyl-d_{10}) at 100 μg mL^{-1} in *n*-nonane, were also purchased from Chem Service Inc. Individual stock solutions were prepared from solids dissolved in pesticide grade hexane (Fisher Scientific) to 100 μg mL^{-1}. Standard mixtures at 1.0 μg mL^{-1} were prepared in pesticide grade hexane from individual stock solutions and were stored at −4 °C. Suitable calibration standards were prepared by dilution of a standard mixture and internal standard (IS) with pesticide grade hexane with a final concentration of IS parathion-d_{10} of 10 μg L^{-1} and diazinon-d_{10} of 30 μg L^{-1} in all standards and samples. The calibration range examined was 0.01−100 μg L^{-1}. All final diluted standards and samples were prepared on the day of analysis. All organic solvents used in standard preparation and pressured solvent extraction (hexane, methanol, acetone, and ethyl acetate) were pesticide grade (Fisher Scientific).

Polyurethane foam plugs (PUFs), 2.54 and 5.08 cm lengths, and glass fiber filters (10.2 cm diameter) were obtained from Pacwill Environmental (Grimsby, ON, Canada); and sorbents were Amberlite XAD-2 from Supelco (Oakville, ON, Canada) and Tenax-TA, 60/80 mesh, from Mandel Scientific Co. Inc. (Guelph, ON, Canada). All PUF and sorbent materials were cleaned prior to sampling by extraction with ethyl acetate and acetone with the same method described in the sample collection and preparation of the air extracts section.

Sample Collection and Preparation of Air Extracts. Weekly air samples were collected during the period of May 2004−December 2005 using a PUF high-volume air sampler (Tisch Environmental, Cleves, OH) with a typical air volume of 2700 m^3. The sampling module contained the PUF/sorbent cartridge (for gas-phase fraction) and a glass fiber filter (for particle fraction) and was prepared at the University of Regina and shipped to Abbotsford, BC. For the collection of gas-phase pesticides, the PUF/sorbent cartridge consisted of 7 g of XAD-2 and 7 g of Tenax-TA sandwiched between a 5.08 cm PUF (bottom) and a 2.54 cm PUF (top). Sampling module changes were performed by Environment Canada staff. Both shipment blanks (not loaded onto PUF sampler) and field blanks (loaded on PUF sampler but no motor operation) showed no detectable levels of fungicides of interest.

Filter or combined PUF and sorbent materials were loaded into 34 or 100 mL extraction cells and extracted with ethyl acetate using an ASE100 or ASE300 pressurized solvent extraction system (Dionex, Sunnyvale, CA). Used were the following extraction procedures: temperature, 100 °C; static mode time, 30 min at 1500 psi; two static cycles; 60% flush volume; purge time with nitrogen (UHP) at the end of 600 s. The total extraction volume was approximately 1.5 times the cell volume. A second extraction with acetone was also tested and showed no presence of these fungicides in the extracts. The organic

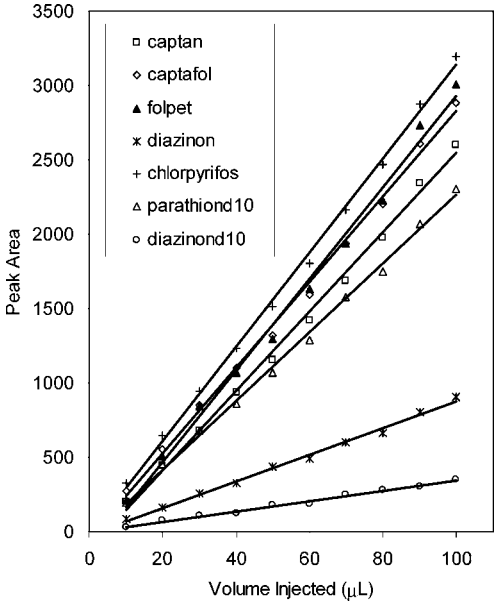

Figure 1. Change in peak area with injected sample size for LVI-COC GC-NCI-MS. Peak area captan and parathion-d_{10} divided by 3; peak area chlorpyrifos divided by 8 for scaling. Standard solution of pesticide mixture at 25 μg L^{-1} captan, captafol, folpet, chlorpyrifos, diazinon, parathion-d_{10}, and diazinon-d_{10}.

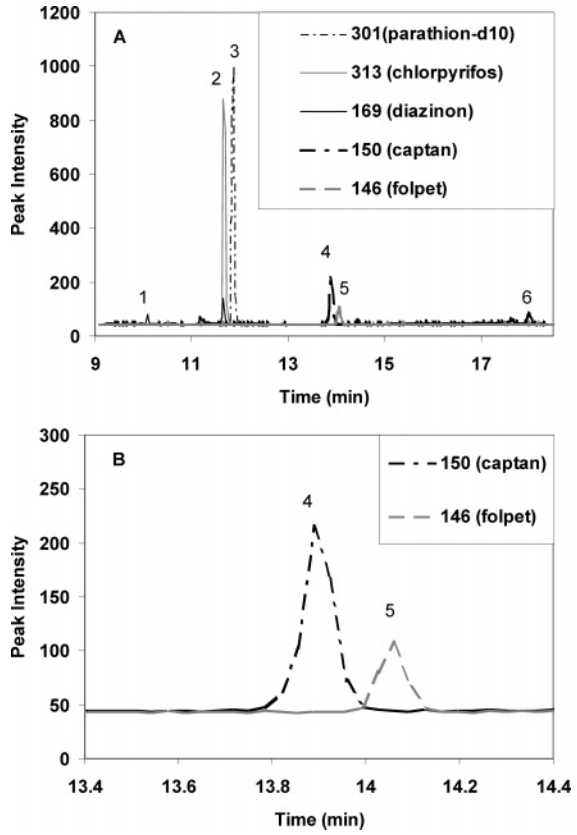

Figure 2. LVI-COC GC-NCI-MS single ion chromatograms of a standard solution of pesticide mixture in *n*-hexane at 5 μg L^{-1} captan, captafol, folpet, chlorpyrifos, and diazinon and 10 μg L^{-1} parathion-d_{10} (internal standard): 1, diazinon (m/z = 169); 2, chlorpyrifos (m/z = 313); 3, parathion-d_{10} (m/z = 301); 4, captan (m/z = 150); 5, folpet (m/z = 146); and 6, captafol (m/z = 150). Solvent delay, 9 min. (**A**) Time scale, 9–19 min; (**B**) expanded time scale, 13.4–14.4 min.

extract in the 250 mL collection bottle from the pressurized solvent extraction was reduced to 3−5 mL in a Visiprep solid-phase extraction

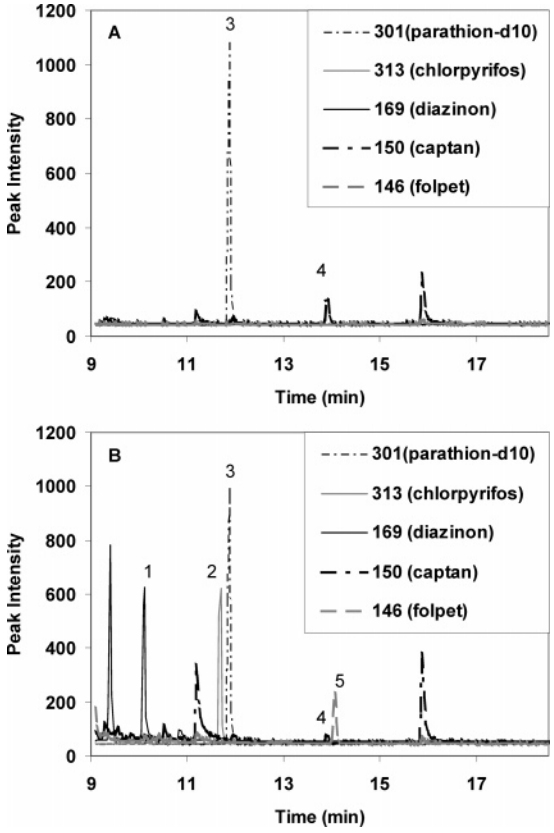

Figure 3. LVI-COC GC-NCI-MS single ion chromatograms of a sample air extract in *n*-hexane. (**A**) Filter extract; (**B**) puf/xad sorbent extract. Peaks: 1, diazinon (m/z = 169) (for **B**, peak intensity divided by 10 for scaling); 2, chlorpyrifos (m/z = 313); 3, parathion-d_{10} (m/z = 301); 4, captan (m/z = 150); 5, folpet (m/z = 146); and no captafol present. Solvent delay, 9 min.

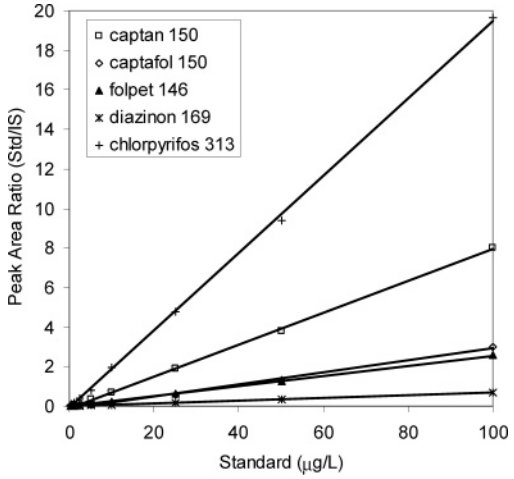

Figure 4. Calibration curve for LVI-COC GC-NCI-MS. Calibration range MDL to 100 μg L^{-1} for injection volume of 100 μL.

(SPE) apparatus, transferred to a 15 mL vial, reduced to near dryness, and redissolved in 0.5 mL of 50/50 v/v% acetone/hexane (pesticide grade) and stored at −4 °C. These sample extracts underwent a number of multiresidue pesticide analysis methods so only a fraction of the extract was available for the fungicide analysis. The use of 50% acetone ensured complete dissolution of all analytes and matrix components in the concentrated extracts stored.

C18 (ENVI-18, 6 cm^3, 1 g, Supelco) SPE tubes were conditioned with 4 mL of ethyl acetate, followed by 4 mL of methanol. Sample extract (0.25 or 0.50 mL) was loaded onto the preconditioned tubes, followed by surrogate standard (diazinon-d_{10}) and methanol such that

Table 2. MDL and LOD for LVI-COC GC-NCI SIM Method and LVI-COC GC-EI SIM Method

description	captan	captafol	folpet	diazinon	chlorpyrifos
MDL NCI-SIM	2.5	5.0	2.5	2.5	1.0
LOD NCI-SIM	1.3	3.6	1.0	1.0	0.5
MDL EI-SIM	10.0	25.0	200.0	5.0	10.0
LOD EI-SIM	7.1	16.3	187.0	1.0	8.0
R^2 linear range NCI MDL–100 μg L^{-1}	0.9999	0.9980	0.9994	0.9998	0.9997
slope NCI MDL–100 μg L^{-1}	8.25E–2	3.02E–2	2.75E–2	5.01E–3	2.11E–1
intercept NCI MDL–100 μg L^{-1}	–1.35E–1	–1.33E–1	–5.41E–2	–2.00E–5	–3.89E–2
R^2 EI-SIM linear range MDL–100 μg L^{-1}[a]	0.9986	0.9910	0.9963	0.9988	0.9992

[a] For folpet, linear range MDL to 1000 μg L^{-1} with EI detection.

the total volume was 1 mL. The eluted solvent collected into fraction F0 was observed to contain no fungicides of interest. The fungicides were eluted with 4 mL of ethyl acetate in the next fraction (F1), and the Visiprep drying attachment (Supelco) was also used to evaporate and concentrate eluted extracts from SPE (and from ASE) to near dryness with nitrogen (UHP). The dried ethyl acetate fraction was redissolved in 0.25 mL of pesticide grade hexane/acetone (50/50 v/v %) and stored at −4 °C. Surrogate recoveries were 85−105% within batch recoveries of ±5% (20 samples). As yearly trends of air concentrations are examined, there was a wide variation in sample concentration; consequently, the dilution factor selected for preparation of the injected sample depended upon sample concentration and presence of matrix components. To conserve sample extract, typically, the first analysis was completed with a dilution factor of 10 or 20 μL sample extract in a total volume of 250 μL, but for lower concentration, samples up to 100 μL/200 μL were used with the addition of IS, parathion-d_{10}, for GC-MS analysis. As there is no 2004−2005 usage or specific application information available on the time of year or farm location that these pesticides were applied, estimation of pesticide levels in air prior to analyses was not possible.

GC-NCI-MS Conditions. The GC-MS system consisted of an Agilent HP6890 GC coupled to a quadrupole mass spectrometer (5973 Network) with EI and NCI capability (turbo performance pump). The GC system was equipped with an Agilent COC inlet with SVE accessory. The COC inlet was connected to ∼1−1.5 m × 0.53 mm i.d. (Siltek deactivated guard column, Chromatographic Specialties, Inc., Brookville, ON, Canada) and then with a Siltek universal connector to a short precolumn (∼0.4 m × 0.25 mm, Siltek deactivated guard column, Chromatographic Specialties, Inc.) to protect the analytical column from build-up of nonvolatile material. This was connected with the SVE (50 μm bleed restrictor, Agilent) and to the analytical column (DB5MS, 5% polydiphenyl−95% dimethylsiloxane, 30 m × 0.25 mm i.d. and 0.25 μm film thickness (J&W Scientific, Folsom, CA) with a Siltek angled Y connector. The oven temperature program was 65 °C for 1 min, 25 °C min^{-1} to 260 °C, 1 °C min^{-1} to 265 °C, 25 °C min^{-1} to 285 °C, hold for 3.8 min, 25 °C min^{-1} to 285 °C, and hold for 3.8 min. The carrier gas was helium (UHP) at 1.0 mL min^{-1}. The COC inlet temperature was set to follow the oven temperature program, with split vent exit (SVE) held open from start of injection to 30 s from start of run. The chemical ionization (CI) gas was methane (99.99%) at 2 mL min^{-1}, the ion source temperature was 150 °C, the quadrupole temperature was 150 °C, and the interface temperature was 290 °C. In EI, the ion source temperature was 230 °C, the quadrupole temperature was 150 °C, and the interface temperature was 290 °C. CI tuning was determined with PFDTD (perfluoro-5,8-dimethyl-3,6,9-trioxidodecane), and EI tuning was determined with PFTBA (perfluorotributylamine). Spectra were obtained at 70 eV for EI and 190 eV for NCI with a dwell time of 100 ms in SIM. The ions selected for identification and quantification in SIM mode for both EI and NCI are shown in **Table 1**. A LEAP Technologies (Carrboro, NC) autosampler equipped with a 100 μL syringe was used for injections at a rate of 1.0 μL/s.

RESULTS AND DISCUSSION

To permit LVIs with the COC inlet, the time that the SVE is open from the start of injection must be optimized. For a 100 μL injection, the response reaches a maximum near 30 s for SVE open time as reported for analysis of other compounds by COC-LVI (*26*, *27*). The 0.53 mm retention gap length of ∼1−1.5 m retention gap was adequate for a 100 μL injection volume and to prevent build-up of nonvolatile materials in the analytical column. The initial oven temperature program was chosen at 65 °C near or just below the boiling point for hexane similar to previous studies (*26*, *27*). The oven temperature program remained at 65 °C during the period when the SVE was open; higher temperatures resulted in significant loss of signal for the fungicides.

Figure 1 shows that peak areas linearly increase with injection volume 10−100 μL (100 μL syringe used). Injection volumes <100 μL may be desirable for dirty matrixes in order to prolong column life. With 100 μL injections of diluted sample extract, approximately 40−60 air extracts and standards could be analyzed without maintenance of the retention gap. The dilution factor used for sample analysis generally varied from 10 μL in 250 μL to 100 μL of sample in 200 μL, but if a dirty matrix is still present after SPE cleanup, reduced lifetime of retention gap can be observed by loss of sensitivity particularly for captan and captafol.

Figures 2 and **3** show the GC-NCI-MS/SIM chromatograms for 100 μL injection of the standard containing 5 μg L^{-1} each of captan, captafol, folpet, diazinon, chlorpyrifos, surrogate standard (diazinon-d_{10}), and IS (parathion-d_{10}) in a standard and in an extracted air sample. Satisfactory resolution is obtained for all analytes and IS from potential interfering components in samples. Of the pesticides examined, only captan had significant levels in the particle phase (filters) as shown in **Figure 3A**. The major portion of the pesticides was observed in the gas-phase fraction (PUF/sorbent extract) with folpet, diazinon, and chlorpyrifos as shown in **Figure 3B**. Although there is potential for long-range atmospheric transport of captafol from usage in the United States, it was not detected in any air samples. The m/z values for captan and captafol in NCI mode shown in **Figure 1** are higher than in EI mode (m/z = 79) and are less prone to interference problems. Similarly, chlorpyrifos can be more prone to interference issues in EI mode (m/z = 199, 197) as compared to NCI (m/z = 313, 315) due to sample matrix.

Figure 4 shows a typical calibration curve with LVI-COC GC-NCI-MS. **Table 2** shows the calibration data in both NCI and EI modes using LVI-COC GC-MS detection. Linear ranges from MDL to 100 μg L^{-1} were observed with good linearity

Table 3. Concentration Ranges for Selected Pesticides in Air Samples Taken from Abbotsford, BC, from May 2004 to December 2005

pesticide	detection limit expressed as air concn[a] (pg/m^3)	concn range for samples above detection limit (pg/m^3)	percentage of samples with detectable levels < 100 pg/m^3
captan	1.8	32–4860	29
folpet	3.8	22–4880	41
diazinon	1.8	44–28580	23
chlorpyrifos	0.8	10–264	93

[a] On the basis of 2700 m^3 air volume, extract dilution factor of 50 μL sample extract in 200 μL total volume for LVI, total extraction volume of 0.5 mL, and MDL for NCI (see **Table 2**).

($r^2 > 0.998$) using peak area ratios relative to the IS (parathion-d_{10}). A linear calibration curve can be obtained for higher concentrations (evaluated up to 7000 μg L^{-1}), but air samples are generally below 100 μg L^{-1}. Method detection limits (MDLs) were calculated from the lowest concentration on the calibration curve whose percent difference of response of pesticide was estimated to be <10% of value from best-fit line. With 100 μL injections, MDLs were 2.5 μg L^{-1} for captan, folpet, and diazinon, 5.0 μg L^{-1} captafol, and 1.0 μg L^{-1} for chlorpyrifos. Limits of detection (LODs) for the instrument were based upon the concentration determined from calibration plots using three times the signal-to-noise ratio obtained from 10 blank solvent samples (**Table 2**). LODs are generally approximately half the value of the MDLs. Analysis with LVI-COC GC-MS (**Table 2**) shows that with a 100 μL injection, MDLs for the fungicides were higher in EI than NCI and for folpet (m/z = 260 EI; m/z = 146 NCI) significantly above the desired range needed for air sample extract analysis of <100 μg L^{-1}.

Table 3 shows the estimated detection levels for these pesticides in air samples based upon a typical air volume of 2700 m^3 and a conservative dilution factor for preparation of sample for injection of 50 μL in 200 μL total volume. All detection limits are much lower (<4 pg/m^3) than the desired goal of <100 pg/m^3. For those air samples collected during May 2004−December 2005 with levels above the detection limit, this method allows reporting of concentrations <100 pg/m^3 in 23−93% of the samples depending upon the pesticide. The highest levels were observed for diazinon, which at these high levels could be analyzed with standard splitless injection. Maximum levels reported for captan and folpet are similar, and much lower levels are observed for chlorpyrifos. On the basis of 2003 BC usage, both diazinon and captan are known to be major pesticides used on berry crops as compared to chlorpyrifos (*24*). Although no available usage information is available for folpet, this analysis confirms its usage in the region. Further analysis for potential for movement of these pesticides by long-range atmospheric transport from agricultural source regions outside of BC is still under investigation.

ABBREVIATIONS USED

COC, cold on-column; EI, electron impact; GC-NCI-MS, gas chromatography−negative chemical ionization−mass spectrometry; LOD, limit of detection; LVI, large volume injection; MDL, method detection limit; NCI, negative chemical ionization; SIM, selective ion mode; SPE, solid-phase extraction; SVE, solvent vapor exit.

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