



## Product Sampling – Aerosol Cans

### 1.0 PURPOSE

To establish standard procedures for obtaining representative test portions of products packaged in aerosol cans.

### 2.0 SCOPE

These procedures are to be used when sampling aerosol products that are brought into the PF laboratory as official samples.

### 3.0 DEFINITIONS

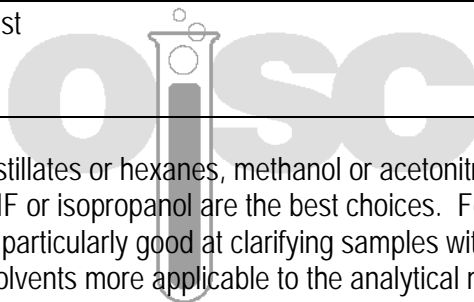
Abbreviations used:-

GC	Gas Chromatography
LC	Liquid Chromatography
OISC	Office of Indiana State Chemist
OTT	Off-The-Top sampling procedure
PF	Pesticide Formulation
QC	Quality Control
SOP	Standard Operating Procedure
TE	Total Exhaust sampling procedure
THF	Tetrahydrofuran

### 4.0 PROCEDURE

#### 4.1 General guidelines.

- 4.1.1 Many pesticide products marketed for home use are packaged in pressurized cans containing a petroleum solvent or water plus an emulsifier as the carrier for the active ingredient (Reference 6.1). Some aerosol products consist of a can with a foil pouch containing the formulated product surrounded by carbon dioxide, which acts as the propellant. **If the product label identifies carbon dioxide as the propellant, the claimed active ingredient statement does not include propellant.** In all other products in which the propellant and formulation are mixed, the claimed concentration of active ingredients includes the weight of propellant.
- 4.1.2 Pesticide investigators are required to sample three aerosol cans from the same lot number as a single official sample. One can is reserved as a split sample in case the product fails to meet label claim. The remaining two cans are available for "Off the Top" (OTT) sampling and "Total Exhaust" (TE) sampling respectively. The initial analysis is performed using OTT sampling. If the product does not meet label claim, the analysis is repeated using TE sampling. If three cans from the same lot number are unavailable, a single can is sampled by TE and if the product fails to meet label claim, the investigator is asked to obtain more cans from the same lot number for further analysis. Single-use "bomb" type products are sampled by TE only.
- 4.1.3 Solvent choice is affected by the presence of petroleum distillates or hexanes in the product, and this information is usually given on the product label. For samples containing



petroleum distillates or hexanes, methanol or acetonitrile are not miscible. For LC analyses, THF or isopropanol are the best choices. For GC, acetone or THF usually work well. THF is particularly good at clarifying samples with high water content. Further dilutions in solvents more applicable to the analytical method can be performed later. To test for solvent miscibility, set up a series of solvent choices in disposable test tubes and release product into each tube. Shake the tubes and observe behavior of the mixtures. The solvent giving the clearest solution will be the best choice.

#### 4.2 Off the Top (OTT) sampling.

4.2.1 The OTT sampling procedure mimics the way that pesticide products are used by the consumer. Aerosol sampling tubes are constructed from 1/8" stainless steel tubing and a ferrule, and are attached to the aerosol can with Tygon tubing after the removal of the plastic spray nozzle. Premade apparatus can be found in the drawer next to the analytical balances.

4.2.1.1 The aerosol is shaken thoroughly to mix the contents. The can is shaken for five minutes on a mechanical shaker, or by hand, and the plastic spray nozzle is removed. A sampling tube is attached to the can at the opening and sample is released by manually depressing the tube. **Note: use the shortest piece of Tygon tubing necessary to cover the nozzle and attach the tube firmly. This reduces the possible contamination of the sample with plasticizers from the tubing.**

4.2.1.2 Always read the use directions on the label. Some aerosols are designed to be used with the can upside down (*eg.* carpet treatment products) and will not sample well when upright.

4.2.1.3 Weigh the unopened can with attached tubing apparatus. An initial portion is released into a glass beaker containing a solvent. Solvent choice is dependent upon the active ingredient and the method of analysis for the active ingredient. The initial portion released is discarded to waste, making sure that enough is released to empty the aerosol tube.

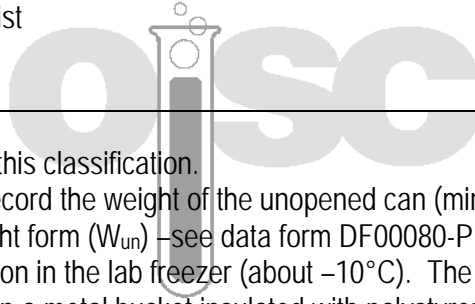
4.2.1.4 The target weight based upon the label claim of the active ingredient is calculated before sampling.

4.2.1.5 The can is then reweighed and the weight recorded in the lab notebook. Put enough extractant into a clean volumetric flask, enough that the tubing end is immersed. A test portion of sample is released into the volumetric flask into the solvent. This can be tricky, as the pressure *may* cause the solvent to splash up the neck of the flask.

4.2.1.6 The can is reweighed and the difference in weights is the weight of the test portion. Any internal standards required are added to the test portion at this time, and the sample is diluted to volume with extractant. A second test portion may be prepared if there is no QC sample for the active ingredient or where necessary. The can that has been sampled is labeled "OTT", with the date and initials of the chemist.

#### 4.3 Total Exhaust (TE) sampling.

4.3.1 The method of total exhaust sampling used is the freezing can method (see reference 6.4). The entire sample is frozen in the can and removed to a storage bottle. The presence of single or multiple phases is determined and the method used to remove a test portion is



based upon this classification.

4.3.1.1 Record the weight of the unopened can (minus cap and any straws, etc) on the aerosol weight form ( $W_{un}$ ) –see data form DF00080-PF. Freeze the can overnight in the upright position in the lab freezer (about  $-10^{\circ}\text{C}$ ). The next morning, prepare an acetone / dry ice bath in a metal bucket insulated with polystyrene.

4.3.1.2 Get a stainless steel pot and wrap it in the blue laboratory diapers for insulation and place it in a fume hood. Purchase approximately 8 pounds of dry ice from the storeroom. Pour approximately 1L of bulk acetone over several blocks of dry ice in the pot. **Take safety precautions when using dry ice. The acetone will boil on initial contact with the dry ice.** The bath is ready when extra pieces of dry ice do not cause boiling when added (temperature about  $-78^{\circ}\text{C}$ ).

4.3.1.3 Insert the can from the freezer and cover with a blue pad for insulation. Leave to freeze for about 120 minutes. Larger cans should be frozen for a longer time. Check and see if the entire sample is frozen. Sometimes single phase aerosols may not freeze at all even after sitting in the acetone/dry ice bath for a long time. Use great care to proceed to the next step should this be the case.

4.3.2 In the fume hood, remove the frozen can (use gloves) and lay the can on the wooden frame.

4.3.2.1 Taking great care, puncture the frozen can along the top shoulder of the can using an awl and hammer. Making two holes close to each other will help later when the can needs to be cut open.

4.3.2.2 Stand the can upright inside a glass beaker at the back of the hood and cover with a second glass beaker. When the hissing sound is no longer heard or no draft can be felt (sometimes, it can take up to 2 hours for all the propellant to be released), record the weight of the can on the aerosol weight form ( $W_{ex}$ ). Alternatively, the can may be left overnight in the hood to ensure that all propellant has escaped, as long as the hood is sealed with a custody seal.

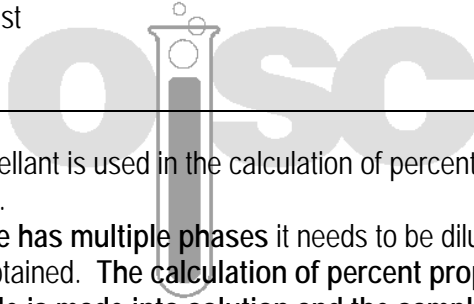
4.3.2.3 Remove the top of the can using either a can opener or tin snips and a stainless steel gauntlet. Put the gauntlet on the opposite hand the is using the snips. **The gauntlet will protect your hand if you slip with the tin snips.**

4.3.3 Weigh a clean and empty wide-mouth 500mL storage jar and lid (Teflon-lined) and record the weight,  $W_j$ .

4.3.3.1 Transfer the entire can contents (including contents of the aerosol tube) to the storage jar. If the sample is a single phase it will pour out easily. If the sample is frozen it is most likely in multiple phases and the can may be warmed in hot tap water to facilitate melting.

4.3.3.2 Record the weight of the empty can (including the removed top and tube) on the aerosol weight form ( $W_{can}$ ). Record the weight of the sample in the jar on the aerosol weight form ( $W_{j+s}$ ).

4.3.4 **If the sample is single phase**, bath-sonicate the jar without the lid for 10 minutes to remove any remaining propellant. Reweigh the sample in the jar and record on the aerosol weight form ( $W_{son}$ ). These weights enable the percent propellant to be calculated. Test portions may be removed directly from the jar and weighed as if a liquid product. The



percent propellant is used in the calculation of percent active ingredient as shown below in section 4.4.2.

- 4.3.5 **If the sample has multiple phases** it needs to be diluted in solvent until a single phase solution is obtained. **The calculation of percent propellant is not required because the entire sample is made into solution and the sample weight ( $W_{ts}$ ) is the  $W_{un}-W_{can}$ .** The test portion is measured by volume after the concentration of active ingredient in the solution is determined using the label guarantee.

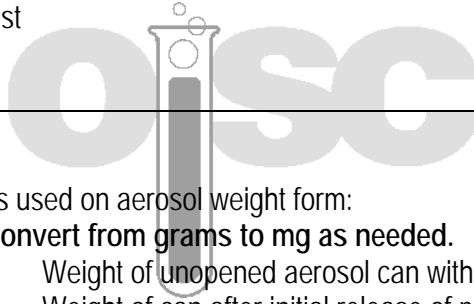
4.3.5.1 The contents of the sample jar are quantitatively transferred, using 100mL of isopropanol, to a 1L volumetric flask. The solvent added is recorded on the bottom of the aerosol weight form. THF is then added in 100mL aliquots, with swirling, until a clear solution is obtained. Sometimes small amounts of hexane (50-100 mL) can help clarify the solution. Switch back to IPA if a couple hundred mL of THF has been added and solution becomes either cloudier than before or the top phase becomes larger. Dilution up to 2L may be necessary to clarify the solution, and other solvents may be tried, but are not common.

4.3.5.2 **Take care to estimate the concentration of active ingredient in the diluted solution so that the target concentration required for the analysis is achievable.** Record the total volume used to make a clear solution on the aerosol weight form, along with the volume of each solvent added. Calculate the concentration of active ingredient in the solution using the total weight of the sample ( $W_{ts}$ ) and the total volume used for dilution ( $D_u$ ).

$$\text{Active Ingredient (in mg/mL)} = (W_{ts} / D_u) \times (\% \text{ label claim} / 100)$$

4.3.5.3 Often, further dilution of the solution is required to prepare a test portion at the target concentration. If internal standard is used in the analysis, add it to the test portion here.

$$\text{Total dilution} = \frac{\text{Total mL of aerosol solution} \times \text{mL of test portion}}{\text{mL of aliquot volume}}$$



#### 4.4 Calculations

##### 4.4.1 Abbreviations used on aerosol weight form:

**Be sure to convert from grams to mg as needed.**

$W_{un}$	Weight of unopened aerosol can with plastic cap removed
$W_{ex}$	Weight of can after initial release of propellant
$W_J$	Weight of empty storage jar (including lid)
$W_{J+S}$	Weight of sample in jar sealed with lid
$W_{Son}$	Weight of sample in jar sealed with lid after 10 min sonication
$W_{Sample}$	Weight of sample in jar ( $W_{Son} - W_J$ )
$W_{prop}$	Weight of propellant = ( $W_{un} - W_{ex}$ ) + ( $W_{J+S} - W_{Son}$ )
$W_{can}$	Weight of empty can
$W_{ts}$	Weight of total sample = $W_{un} - W_{can}$ or $W_4 + W_{prop}$

##### 4.4.2 **Calculations for single-phase aerosols that are sampled by TE.**

###### 4.4.2.1 Calculation of the percent propellant in the aerosol

$$\% \text{ Propellant} = (W_{prop} / W_{ts}) \times 100$$

4.4.2.2 When a test portion of a single phase aerosol that has been sampled by TE is analyzed, the test portion no longer contains propellant. The percent propellant calculated in 4.4.2.1 is used to correct for this.

4.4.2.3 Target weight of the test portion needed for analysis, can be calculated as follows:

$$\text{Target Weight (in mg)} = \frac{\text{Conc. of Level 3 standard (mg/mL)} \times \text{Dilution (mL)}}{\% \text{ Label Claim} / (100 - \% \text{ Propellant})}$$

4.4.2.4 To report out % Active Ingredient found the correction can be applied to the calculated percent active ingredient as follows:

$$\% \text{ Active ingredient}_{\text{corr}} = \% \text{ Active ingredient found} \times [(100 - \% \text{ propellant}) / 100]$$

**Note: % Active ingredient only needs to be corrected for single phase aerosol.**

##### 4.4.3 **Calculations for multi-phase aerosols that are sampled by TE.**

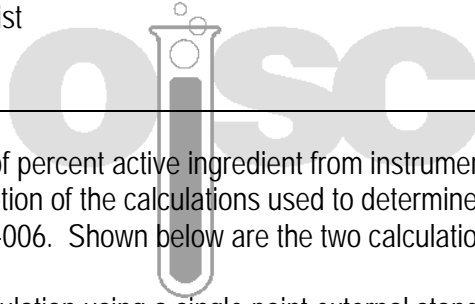
###### 4.4.3.2 Calculation of the total sample weight:

$$W_{ts} = (W_{un} - W_{can})$$

###### 4.4.3.3 Theoretical concentration after addition of solvent:

$$C_{\text{theo}} = (W_{ts} * \% \text{ Label Claim}) / \text{Final Du}$$

Final Du = final size of volumetric flask (typically 1000 or 2000mL)



4.4.3 Calculation of percent active ingredient from instrumentation.  
A full description of the calculations used to determine percent active ingredient is given in SOP DH-PF-006. Shown below are the two calculations most commonly used in the laboratory.

4.4.3.1 Calculation using a single point external standard.

$$\% \text{ Active ingredient} = \frac{R_u \times W_s \times D_u}{R_s \times W_u \times D_s} \times \% \text{ purity}$$

Where R=instrument response            u=unknown sample  
W=weight                                      s=standard  
D=dilution

4.4.3.2 Calculation using a linear standard curve.

$$\% \text{ Active ingredient} = \frac{Y - b}{m} \times \frac{D_u}{W_u} \times 100$$

Where Y=plotted response            u=unknown sample  
b=y-intercept                              D=dilution  
m=slope of curve                          W=weight

**5.0 ATTACHMENTS**

None.

**6.0 REFERENCES**

- 6.1 Sampling of insecticides from pressurized cans: Collaborative study, Y. Kawano, JAOAC **62**: 494 (1979).
- 6.2 Analytical studies of pyrethrin formulations by gas chromatography: Isolation of the pyrethrins from water-based formulations, Kawano, V. & Bevenue, A., J. Chrom **72**: 51 (1972)
- 6.3 Agriculture Canada methods book, section 3.4.6.1
- 6.4 Pyrethrin and piperonyl butoxide in pesticide formulations, AOAC 982.02, OMA 16<sup>th</sup> ed. Chapter 7 pg. 48 (1995).
- 6.5 DF 00080-PF: Aerosol Sample Weight Form

Reviewed by: \_\_\_\_\_

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