Determination of Pesticides in Food Samples: Fruit and Vegetables Utilizing the DryVap® Concentrator System with High Boiling Solvent Mixtures

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Introduction

Many applications require samples to be extracted with organic solvents which can have fairly high boiling points. These higher boiling solvents can cause several problems, the biggest one being that most evaporative equipment might have difficulty achieving the sufficiently high temperature required to evaporate these solvents. Even if the equipment can evaporate higher boiling solvents, the older equipment designs being used, could translate into excessively long evaporation times.

This study was conducted to evaluate the DryVap® Concentrator System’s ability to work with a high boiling solvent mixture. The mixture used for this study is used for Method S-19; a general method used for the determination of pesticides in food samples (fruit and vegetables). 45 mL of a solvent mix, containing 55% iso-octane, 28% toluene, 11% acetone, and 6% hexane was evaporated on the DryVap®. The DryVap® System was able to concentrate the solvent from 45 mL to 0.9 ml in approximately 14 minutes. Recovery values for several pesticides from this solvent mix was also conducted.

Instrumentation

- Horizon Technology DryVap® Concentrator System
- Agilent 5890 Series II GC/ECD
- GC Racer, Zip Scientific

Method Summary

1) The following mixture was prepared:
   a. 275 mL of iso-Octane (b.p. = 99.3°C)
   b. 137 mL of toluene (b.p. = 110.6°C)
   c. 55 mL of acetone (b.p. = 56°C)
   d. 28 mL of hexane (b.p. = 69°C)
2) 45 mL of this mix was placed into an evaporator tube.
3) Main vacuum set to 15” Hg.
4) Nitrogen gas pressure set to 20 psi.
5) Heater Power set to 5 (100% power) = 60 watts.
6) Auto Rinse Mode set to 0.
7) Sparge Heater set to 88.
8) Final analysis by GC-ECD.

Results

The DryVap® Concentrator System uses vacuum, internal heat, and nitrogen sparge gas to evaporate the solvent. The use of an internal heater is unique in the DryVap®, in that the heat is applied directly to the solvent, vs. conduction through the glass walls of the evaporator tube via a water bath or external heat source. The use of individual internal heaters provides faster heating and cooling cycles, allows different solvents to be evaporated simultaneously (i.e. different boiling points), and allows the heater to be turned off during the final gas sparge cycle, resulting in better recoveries for volatile compounds.

It is also important to note that because the DryVap® evaporator tubes are run under vacuum, typically at 15” Hg, the boiling points of all solvents are lowered considerably. See Chart 1. This will aid in reducing the total evaporation times.

![Chart 1 Boiling Point as a Function of Vacuum](image)
To ensure the heater turns off properly as the solvent level approaches the top surface of the heater, the software algorithm and an embedded thermocouple senses the rise in temperature, and turns the heater off before the heater coil is exposed. A typical run using 45 ml of Methylene Chloride is shown in Chart 2.

The blue line (Therm) shows the plot of the thermocouple as the methylene chloride is evaporated. At time zero when the run is started the thermocouple is cool, and so the output is at zero. As the heater begins to heat, the thermocouple value begins to rise. Within a few seconds, the thermocouple reaches a stable value. It is important to remember, that because the evaporation tube is under vacuum, the boiling point of the solvent is lowered from 39°C to approximately 21°C. Likewise, the thermocouple value is also lowered accordingly. It should be noted that the Y axis scale is not degrees C, but an arbitrary scale.

Two preset values are used to determine when the heater should be turned off; a Delay Value (T12) which is used to determine when to begin recording the Moving Average (MA) value, and an Offset Value (T13). For this run, the Delay Value preset of 60 seconds was used. This can be seen on Chart 2 as both the MA and Thresh signals begin at 60 seconds. The MA is a “box car” type of moving average calculation, such that as each new value is recorded, the last value is dropped. When the Delay Value timer is reached, the current thermocouple value is recorded, and fills 90 registers. This “weighted” value is used as the MA and this process smoothes out the thermocouple signal and becomes the reference value to which the Offset Value is added. The Offset Value of 130 is preset at the Factory using methylene chloride, but can be reprogrammed by using the Learn Mode.

Referring to Chart 2, when the solvent level begins to fall below the thermocouple (at approx 320 seconds), the thermocouple begins to rapidly warm, and the output signal rises quickly (referred to as “lift off”). When the thermocouple value finally reaches the Thresh value, the heater is turned off. This occurred at approximately 340 seconds. The thermocouple then begins to cool and the drop in the output signal is seen.

Chart 3 shows a typical run using 45 mL of hexane. All preset values were used, and the heater turned off while the heater coil was still immersed in the solvent. Note that the thermocouple signal reached a higher Y axis value (approximately 100), while Methylene Chloride only reached a value of 25, and that it took almost one minute for the thermocouple value to stabilize (vs. a few seconds for methylene chloride). When the thermocouple value reaches the threshold value, the heater turns off. With pure solvents, the heater will turn off at the proper time, leaving the heater coil covered with the solvent.

Next, 45 mL of the S-19 solvent mix was evaporated. Since this is a mixture of 4 solvents, 2 of which are fairly high boiling, experience has shown that the Learn Mode should be used to properly program the heater. However, as the purpose of this test was to determine what the optimal parameters should be when using this mix, the normal presets were used, and the data recorded. See Chart 4 for the output responses of this mixture.

When the solvent was at the desired level above the top surface of the heater coil, the heater was manually turned off. This occurred at 460 seconds into the run. However, as can be seen, there is almost no “lift off” of the thermocouple output, indicating that the heater was turned off prematurely.
In addition, the Offset Value of 130 is too high to be used for this solvent mix. With the Threshold value this high, the solvent level would have passed below the heater coil and low recovery values would have resulted.

The Learn Mode was then used for the next run of the S-19 solvent mix. Prior to this run, the Minimum Offset value (T37) was changed from the preset value of 60 to 5. This lower Minimum Offset value will now allow the station being programmed to accept a lower Offset Value (T13). The sample was then run. See Chart 5 for the results.

The new Offset Value calculated by using the Learn Mode automatically adjusted the Offset Value to 30 (from the previous value of 130). As can be seen in this chart, the “lift off” was very pronounced and the heater turned off while the solvent level was still above the heater coil. This was a successful run.

Looking at Chart 5, first, note that the time required for the thermocouple to stabilize takes about 270 seconds. This is due to the presence of the high boiling solvents. Because the Moving Average data is based on the thermocouple output, the Moving Average value now lags behind the actual thermocouple value. Eventually, the Moving Average value catches up, but not until 330 seconds into the run.

Chart 6 shows the data where the Delay Value T12 has been increased to 360 seconds. Now the Moving Average starts when the thermocouple output is stable. This smoothing of the MA value helps ensure proper heater shut off.

Once the Delay Value T12 (changed from 60 to 360 seconds) and the Offset Value T13 (changed from 130 to 30) had been made, a spiked mixture of the S-19 solvent was run. The results are shown in Table 1.

Table I. Average Recovery Values Of Selected S-19 Compounds

<table>
<thead>
<tr>
<th>Peak</th>
<th>Compound</th>
<th>Average</th>
<th>RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Aldrin</td>
<td>83.0</td>
<td>1.4</td>
</tr>
<tr>
<td>2</td>
<td>4,4'-DDE</td>
<td>82.7</td>
<td>1.2</td>
</tr>
<tr>
<td>3</td>
<td>Endosulfan I</td>
<td>81.7</td>
<td>3.0</td>
</tr>
<tr>
<td>4</td>
<td>Endosulfan Sulfate</td>
<td>79.1</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>Mixture Average</td>
<td>81.6</td>
<td>2.1</td>
</tr>
</tbody>
</table>

Conclusions

The purpose of this study was to determine the optimal parameters settings for the DryVap® Concentrator System when using high boiling solvents, as required in Method S-19. In order to ensure the heater turns off while the heater coil is still immersed in the solvent, the Moving Average Delay Timer (T12) was changed from the preset value of 60 to 360. This will ensure that the Moving average value is closer to the actual thermocouple value. In addition, the Offset Value (T13) needs to be set to a new value of approximately 30. The lower the T13 value (adding the MA and the Offset Values together, equals the Threshold Value), the lower the Threshold value which means the thermocouple will trip sooner, shutting off the heater at the proper time.

Making the two changes to the DryVap® parameters ensured the heater turned off properly, allowing the System to easily handle the high boiling solvent mixture required by the S-19 Method. The time to evaporate 45 mL of this solvent mix took approximately 12 to 14 minutes, and provided satisfactory recovery values.