California Department of Food and Agriculture's Center for Analytical Chemistry Memoranda Addressing MITC Field Spike Recoveries

State of California

Memorandum

To: CDPR-Environmental Monitoring Section
Place: Sacramento, CA

Date: May 09, 2018

From: **Department of Food and Agriculture** --

Stephen Siegel
Senior Environmental Scientist
Environmental Safety laboratory

Subject: Addressing the recovery of MITC from charcoal tubes

In a meeting with the CDPR air network group it was discussed that the overall average recovery for our ongoing spikes associated with each set is lower than what is expected for the data to meet the user's requirements.
The overall average recovery for the spikes is 75% with the lower acceptable recovery set to 55% and the upper recovery set to 95%.
To better meet the needs of the air network we looked into modifying the extraction technique in order to raise the average recovery to above 80%.
We tried different solvents and solvent combinations along with varying procedures to enhance the overall extraction efficiency.
Our experiments lead us to a twofold modification in the extraction technique.
First, we used a higher concentration of carbon disulfide as a co-extraction solvent and second we employed a more vigorous mixing technique.
We increased the amount of carbon disulfide to 1.0% and we increased the amount of time that we vortex the sample from 20 seconds to 1 minute.
This new extraction technique has raised the overall extraction efficiency to close to 90%.
This method was then validated using 5 levels on 5 days.
The average recovery for this validation is 89.2% with a lower control level of 68.8% and an upper control level of 110%. See attached method validation results in appendix 1.

We are addressing the low recoveries of the blind spikes.
To ensure that the tubes are spikes correctly we are spiking two tubes with the same amount of MITC standard at the same time.
One tube will be kept frozen until delivered back to the lab for analysis while the other tube is sent to the field and set up in an air sampler and pumped for 24 hours. The results of these analysis may help in determining if there is any loss of analyte during the sampling process especially during hot or very humid days. We will evaluate these spike recoveries when the results become available.

Sincerely,

Stephen Siegel

Stephen Siegel
Senior Environmental Scientist (Supervisor)

Appendix 1

Method Validation Data for MITC in SKC 226-02 charcoal tube from GC-MS

Spike Level MITC Spiked (μg)	**Set1** MITC found (%)	**Set 2** MITC found (%)	**Set 3** MITC found (%)	**Set 4** MITC found (%)	**Set 5** MITC found (%)
0.1	101	91.6	98.8	103	99.5
0.2	90.3	95.0	95.1	96.7	93.7
0.5	79.4	89.9	87.6	87.3	86.5
0.7	78.9	83.7	86.9	84.0	84.2
1.0	77.0	87.3	84.4	85.0	84.9

Average	89.3%
Standard Deviation	7.06%
Upper Control Limit	110%
Lower Control Limit	68.1%

State of California

Memorandum

To: CDPR-Environmental Monitoring Section
Place: Sacramento, CA

Date: June 14, 2018

From: **Department of Food and Agriculture** --

Stephen Siegel
Senior Environmental Scientist
Environmental Safety laboratory

Subject: Addressing the recovery of MITC from charcoal tubes

The lab addressed the low recoveries of the blind spikes.
To ensure that the tubes are spikes correctly we are spiking two tubes with the same amount of MITC standard at the same time.
One tube will be kept frozen until delivered back to the lab for analysis while the other tube is sent to the field and set up in an air sampler and pumped for 24 hours. The results of 5 sets of blind spikes from 2/16/18 to 4/3/18 are listed in appendix 1. The results indicate that there is some but minimal loss of analyte during the sampling process. The analyte loss is between 2 and 12%. We will continue to monitor the duplicate blind spike results as sampling is done during the hot summer months to determine if the heat contributes to any analyte loss during sampling.
The low recovery for the blind spikes would indicate that the sampling, extraction and analysis of the samples the lab analyzed during 2017 are reporting findings that are lower than what is actually in the air during the sampling.

Sincerely,

Stephen Siegel

Stephen Siegel
Senior Environmental Scientist (Supervisor)

Appendix 1

Preparation Date	Extraction Date	Sample Number	Pesticide	Spike Level (ug/sample)	Results (ug/sample)	Percent Recovery (%)	Exceed Control Limits
2/16/2018	3/7/2018	E00421	MITC	0.5	0.417	83.4%	NO
2/16/2018	3/7/2018	Z00001	MITC	0.5	0.428	85.6%	NO
2/23/2018	3/7/2018	E00432	MITC	0.6	0.453	75.5%	NO
2/23/2018	3/7/2018	Z00002	MITC	0.6	0.494	82.3%	NO
3/13/2018	3/20/2018	E00450	MITC	0.8	0.672	84.0%	NO
3/13/2018	3/20/2018	Z00003	MITC	0.8	0.771	96.4%	NO
3/22/2018	4/3/2018	E00457	MITC	1.0	0.846	84.6%	NO
3/22/2018	4/3/2018	Z00004	MITC	1.0	0.940	94.0%	NO
4/3/2018	4/16/2018	E00475	MITC	0.50	0.425	85.0%	No
4/3/2018	4/16/2018	Z00005	MITC	0.50	0.450	90.0%	No

Samples with Zxxxxx were stored at West Sac

State of California

Memorandum

To : CDPR-Environmental Monitoring Section
1001 I Street
Sacramento, CA 95814

Date: July 2, 2018

Place: Sacramento

Phone: (916) 228-6840

From : **Department of Food and Agriculture** -

Stephen Siegel
Senior Environmental Scientist
Environmental Safety Lab
3292 Meadow View Rd
Sacramento CA 95832

Subject : **Causes for the Low Recoveries of MITC Field Spikes**

This is a follow up to clarify the memo dated June 14, 2018 regarding the low recovery of MITC in field spikes. The statement that a low recovery in a field spikes relates to lower overall recovery in an air sampling may not be accurate. Ambient MITC may trap (adsorb) differently to charcoal than MITC from a spiking solution.

Generally field spike is used to estimate the effectiveness of the measurement system including sampling during actual air sampling conditions. The field spike will also estimate the performance of extraction and analytical variability of the laboratory sample analysis.
In this case, the field spikes are prepared by adding a known amount of MITC solution to a blank charcoal sampling tube. MITC solution is prepared in 1% carbon disulfide in ethyl acetate solvent. Spiking is done using a syringe that delivers the MITC solution to a localized area near the top of the charcoal in the tube. During air monitoring spiked tube is placed on an air sampler that pumps ambient air through the tube in the sampling period. Also, a blank charcoal tube will accompany the field spike on the sampler during sampling. Under ideal conditions, this technique allows for measuring MITC concentration in the field with confidence if the spiked MITC recovery is within acceptable range. However, it is possible that hot or humid air passing through the charcoal tube moves the volatile ethyl acetate solution resulting in passage, spreading and not binding of MITC to the charcoal throughout the tube which can then contribute to lower trapping efficiency and lower MITC recoveries.

Preparing an MITC field spike using a solution gives it a different characteristic than MITC in ambient air which may not accurately estimate its actual concentration. Thus, the amount of ambient MITC may not be biased low based on the recovery of field spike sample.

Sincerely,

Stephen Siegel

Stephen Siegel