



# Comparison Of Results Humic Acid Methods

California Department of Food and Agriculture



## Humic Trade Association Request

- The Humic Trade Association requested CDFA to consider changing its official humic acid analysis method.
- The HTA contends that the CDFA method allowed for inaccurate, usually inflated, guarantees for humic acid compared to certain other methods such as the Swift gravimetric method. Potentially confounding materials include kelp, NPK fertilizer, coal, molasses and particularly lignosulfonates.



## Background

- CDFA recognizes that humic acids are unlike a traditional chemical with a CAS number.
- In concept, humic acids are complex components of advanced decomposition.
- However, current methods detect a variety of compounds from that decomposition contributing to humic substances



## Objective

- CDFA was attempting to evaluate the use of an ashing step to the CDFA method and consider the impact on existing product registrations. The ashing step is a primary difference between the CDFA method and the modified Swift<sup>1</sup> or Lamar<sup>2,3</sup> methods.

<sup>1</sup>Swift, R.S. 1996. In *Sparks (Ed.): Methods of Soil Analysis. Part 3. Chemical Methods*. SSSA, Madison, WI, pp 1081-1021.

<sup>2</sup>Lamar, R.T., D. Olk, L. Mayhew, P.R. Bloom. 2014. A new standardized method for quantification of humic and fulvic acids in humic ores and commercial products. *Journal of AOAC International*, 97(3): 721-730.

<sup>3</sup>Lamar, R.T. & K.H. Talbot. 2009. Critical comparison of humic acid test methods. *Comm. Soil Sci. Plant Analysis*, 40: 2309-2322.



## Methodology

- Source Material - Fertilizing material products that were sampled by CDFA inspection staff
- Collection - Sampling as part of routine inspector activities – not focused on this study. Thus some were humic only but many were mixed products.
- Processing - When samples arrived at CDFA Chem Lab they were evaluated for presence of a humic acid guarantee. If present, the samples were split.
  - One half used for normal regulatory use employing CDFA method
  - One half used the modified CDFA method = with ashing



## Differences between the methods

- **CDFA method – no ashing**
- **Modified CDFA method – ashed for 2 hours at 600°C.**
- Lamar method - The ashing step is 4 hours at 500°C

### Additional differences

- CDFA method - has a 1.5 hour mixing for solid samples and 0.5 hour mixing for liquid samples. The mixing is done under normal atmosphere.
- Lamar Method - has a 6 hour mixing under N<sub>2</sub> gas headspace



## The Comparisons

- **CDFA method – no ashing**
- **Modified CDFA method – ashed for 2 hours at 600°C.**
- The original goal was to address if the ashing would affect the humic analysis.



## Comparisons of CDFA method -with and without ashing

- 87 Samples
- Humic guarantees varied between 0.06% and 65%
- Some were dry samples and some were liquid.
- Some were humic acid only and some were mixed products.
- A few were by chance sampled by two different inspectors and thus repeated.



## Violations by CDFA Standards

	Number of Samples	% of Total
With original method (without ashing)	15	17.2%
With modified method (with ashing)	21	24.1%
With both – overlap	15	17.2%

Ashing did not eliminate any violations, it would just create more.



## Dry products – mixed with fertilizer (usually home and garden plant foods)

- 31 samples (one was a repeat) = 30 samples
- Humic acid guarantees ranged from 0.9% to 15%
- % Ash ranged from 0.9 to 28.9
- Two violations – both methods
  - Guarantee 4.0 – no ash 3.5, with ashing 3.2
  - Guarantee 4.5 – no ash 3.7, with ashing 2.8
- Ashing will not impact most dry products mixed with fertilizer



## Dry products – Humic Only

### Humic only guarantee or only apparent ingredient

- 16 samples (three were repeats – but major variance between samples on two so including all three)
- Guarantees ranged from 17% to 65%
- % Ash ranged from 20.8 to 32.4
- Violations –
  - Three of sixteen were violation *with no* ash – 19% violation
  - Thirteen of sixteen were violation with ashing – 81% violation
- Ashing will require most dry humic only products to relabel



## Liquid products – mixed with fertilizer (usually home and garden plant foods)

- 6 samples (no repeat) = 6 samples
- Guarantees ranged from 1.4% to 60%
- % Ash ranged from 16.2 to 38.8
- Violations –
  - Two of six were violation *with no* ash – 33% violation
  - Four of six were violation with ashing – 67% violation
- Ashing will require most liquid humic only products to relabel



## Liquid Products – Humic Only

### Humic only guarantee or only apparent ingredient

- 22 samples (four were repeats – but major variance between samples on one so including that one)
- Guarantees ranged from 0.5% to 12%
- % Ash ranged from 20.8 to 32.4
- Violations –
  - Six of nineteen were violation *with no* ash – 32% violation
  - Seventeen of nineteen were violation with ashing – 89% violation
- Ashing will require most liquid humic only products to relabel



## Product Sampled by more than one Inspector

	Label Guarantee	Without Ashing	With Ashing
Firm A -Liquid, humic only	6.0	7.1	5.3
	6.0	6.8	5.2
	6.0	7.1	5.3
Firm B -Liquid, humic only	4.0	2.3	1.7
	4.0	2.3	1.7
Firm C -Liquid, humic only	12.0	6.5	4.9
	12.0	11.1	8.2



## Comments

- A huge percentage of products would require relabeling
- Most dry humic only would have to drop guarantee 5-10% lower than it is now, no one firm greatly impacted more than others
- Most liquid humic only would have to drop guarantee 5-60% lower than it is now, three firms greatly impacted (major % change)
- No dry mixed product would have to drop guarantee that were not already in violation with traditional method
- Some liquid mixed products would have to drop guarantee 10-60% lower than it is now, two firms greatly impacted (major % change)



## Comments - continued

- There does not appear to be a clear benefit to adopting an alternative humic acid methodology
- Most of the products that show the greatest difference between ashing and no ashing are products that have undergone CDFA-OIM on-site inspections and no adulteration with non-humic has been observed.
- A change in method would cause some level of disruption in the industry due to labeling costs, re-registration, etc, as well as potential fines for firms not adjusting labels.



## Comments -continued

- CDFA was not utilizing the complete Lamar method, rather only the most significant divergence from the CDFA method – an ashing step.
- The ashing entails an extra step and causes delays compared to testing with the CDFA method. The Lamar method would add additional time and costs to regulatory state labs that will test for humic acids.
- None of these methods eliminates the “misidentification” of humic acids in lignosulfonates, feather meal and blood meal.



## Comments -continued

- Since the data gathered to date regarding the utility and effectiveness of humic acids was gathered based on products defined by existing methods, how much of that is still relevant with products that would be defined by the Lamar method? A comparison is that a new method for iron would not redefine iron. A new method for humic acid would redefine what is and what is not humic acid.
- Only a limited number of states are willing to do regulatory tests for humic acid, these states would be most impacted by defining that test.