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Analysis of “The Big Four” Heavy Metals in Hops by Graphite Furnace Atomic Absorption and Cold Vapor Mercury

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1: Introduction

Plants concentrate metals by absorbing them from the soil in which they are grown. Some metals are beneficial and essential for life whereas other metals are highly toxic and have negative effects with even the lowest of levels. Because of their toxicity, quantification of these elements is needed. This application will investigate the preparation and analysis for heavy metals in Cascade Hops using Shimadzu AA-7000 with Graphite Furnace Atomic Absorption and Cold Vapor techniques. Spike and Recovery tests are performed at or below the analysis target levels to ensure accuracy and sensitivity of the technique.

Element	Analysis Target PPM	As Prepped (50x dil.) PPB
Lead	1.20	24
Cadmium	0.82	16
Mercury	0.40	8.0
Arsenic	2.00	40

Table 1. Metals Target Analysis

2: Experiment

2-1: Sample Preparation

Cascade Hops were purchased pre-dried and ground. 0.5 grams of Hops were added to a closed vessel digester, and 4 mL of Nitric Acid, 2 mL of 30% H_2O_2, and 1 mL of DI H_2O were added. The sample was ramped to 900 watts over 15 minutes and held for another 20 minutes at that power. The sample was then allowed to cool and brought to 25 mL total volume with DI H_2O.

2 mL of the solution was reserved for analysis of Cd, As and Pb by Graphite Furnace Atomic Absorption. 20 mL of sample was reserved for Hg analysis by Cold Vapor; 10 mL of untreated sample, and 10 mL of sample spiked to 1 ppb Hg.

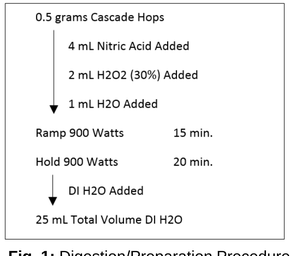

Fig. 1: Digestion/Preparation Procedure

Shimadzu AA-700

2-2: Analytical Method and Conditions

Measurement was conducted using the calibration curve method. The main measurement parameters of the instrument are shown in Table 2. The standard solutions were prepared by diluting commercially available standard solutions for atomic absorption measurement. 100 mL of calibration solution was prepared at 20 ppb As, Pb, 10 ppb Hg and 1 ppb Cd stabilized with 1% nitric acid. Reserve 50 mL for Calibration solution 1. Bring 50 mL of Calibration solution 1 to 100 mL. Reserve 50 mL for Calibration solution 2. Calibration solution 3 was adjusted to account for the lower target levels in Table 1. A similar dilution as the previous scheme could be used.

	As	Pb	Cd	Hg
WaveLength nm	194	283	228	254
Slit Width nm	0.7			
Ignition mode	BG-D2			
Atomization	Electrothermal			Cold Vapor

Table 2: Measurement Conditions

Calibration Solution	1	2	3	Units
As	20	10	4.0	ppb
Cd	1.0	0.5		ppb
Hg	10	5.0	1.0	ppb
Pb	20	10	5.0	ppb

Table 3: Calibration Solutions

3: Results and Conclusion

Figures 2, 3, 4 and 5 show the generated calibration curves for each of the analytes. All calibration curves achieved a good linear coefficient of 0.999 or better, showing the instrument is capable of measuring the specified target range shown in Table 1 and Table 3.

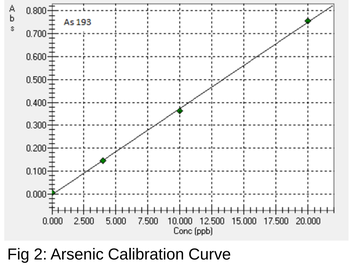

Fig 2: Arsenic Calibration Curve

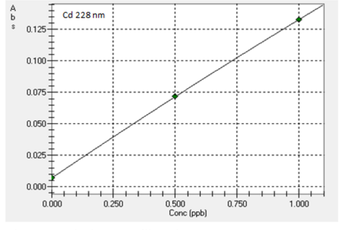

Fig 3: Cadmium Calibration Curve

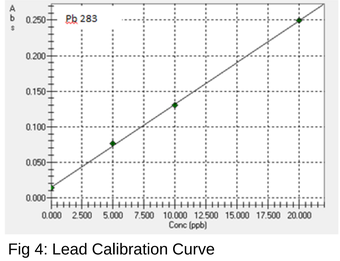

Fig 4: Lead Calibration Curve

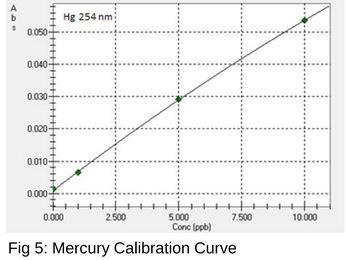

Fig 5: Mercury Calibration Curve

Figures 6 and 7 shows the signals of each analyte of the unknown samples and that of the spikes for As, Cd, Hg and Pb. There is good signal distinction at each of the target analysis levels indicated in Table 1.

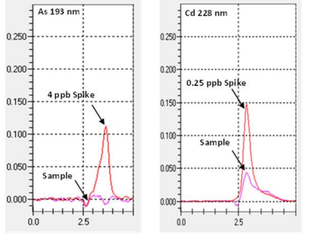

Fig 6: Arsenic & Cadmium Sample and Spike

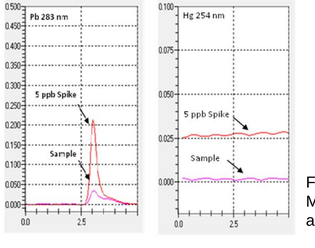

Fig 7: Lead & Mercury Sample and Spike

Element	Sample PPB	Spike PPB	Spike Result PPB	Recovery %
Lead	0.85	5.00	5.98	102.6
Cadmium	0.20	0.25	0.47	109.8
Total Mercury	0.09	5.00	4.96	97.4
Total Arsenic	0.53	4.00	4.71	104.5

Table 4: Results of Sample & Spike

The results in Table 4 show that all of the elements were within the target analysis and the sample spikes achieved recoveries of 90%-110% of their theoretical values. The recoveries show that the system is capable achieving good sensitivity and accuracy at the desired elemental concentration levels.

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