

Mercury Determination in Cabbage, BCR-679, using the CETAC QuickTrace™ M-7500 CVAAS

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INTRODUCTION

Mercury determination in foodstuffs is a crucial part of environmental monitoring. Various forms of mercury from soil, air and surface water results in bioaccumulation in plants as well as other forms of vegetation. Bio-accumulation can occur by absorption of mercury through the plant leaves from the atmosphere or through the soil and into the root system, which can come from agricultural land, municipal sludge and industrial wastes. Soil type, pH, and organic content all affect the amount of mercury that is absorbed into the roots of the plant. The goal of this application note is to validate the QuickTrace™ Mercury Analyzer M-7500 Cold Vapor Atomic Absorbance Analyzer in the low ppt concentration range, by quantitating total mercury in the standard reference material BCR-679, White Cabbage. A modified method was developed to carry-out this specific application.

INSTRUMENTATION



Figure 1. QuickTrace™ M-7500 Mercury Analyzer

The QuickTrace™ M-7500 is a stand-alone independent cold-vapor atomic absorbance spectrometer used to determine total mercury in all different sample types, and is used for quantitative analysis within a large working range. The QuickTrace™ M-7500 is accompanied with an autosampler which allows for hands-free sample-batch analysis, and a four-channel peristaltic pump that guarantees smooth sample delivery into the sample cell along with online sample reduction of inorganic mercury to elemental mercury. The reduced sample flows over the gas-liquid separator where the sample is liberated from the liquid by the carrier gas into the system. The sample is detected by a photovoltaic detector at wavelength 253.7 nm. Data is collected in real-time and recorded on a chart recorder in the QuickTrace™ software. Instrument controls allow for manual control of the lamp, peristaltic pump, argon flow, and smart rinse threshold, by optimizing various instrument parameters results in total mercury analysis over a large dynamic working range is achievable.

The QuickTrace™ M-7500 instrument detection limit is < 0.2 ppt with minimal instrument drift and can be extended to > 500 ppb.

EXPERIMENTAL

This specific application is developed for the quantitation of total mercury in the low ppt range with analysis of BCR-679, White Cabbage. White Cabbage is digested using mercury-free aqua regia, 3:1 (HCl:HNO₃). The carrier gas is set at approximately 120 psi with instrumental flow at 40 mL/min through the system. The certified reference material BCR-679, White Cabbage, is stored in a brown glass bottle with a polyethylene insert and plastic lid. Each bottle contains 15 grams of reference material. The sample is shaken for approximately five minutes prior to sample digestion to ensure sample homogeneity. The tubes are cleaned with dilute detergent, 30% HNO₃, and three ultra-pure mercury-free deionized water rinses. Each sample is digested and analyzed in pre-cleaned 50 mL polypropylene centrifuge tubes. The sample is weighed out into the digestion vials, digested and then brought up to volume with 3% hydrochloric acid. Liberated inorganic mercury is reduced with the excess online addition of 10% stannous chloride in 7% hydrochloric acid. Seven replicates of the standard reference material are analyzed along with the appropriate quality control checks to validate the instrument. Total analysis time is approximately one hour and each sample is analyzed for 200 seconds. A normal linear calibration is analyzed and includes six non-zero standards and one calibration blank. Initial calibration verification and initial calibration blank are analyzed immediately following the calibration and at the end of the sample batch to validate the method calibration. Calibration standards are matrix-matched to the digested samples to minimize biased data. The appropriate aliquots of a 200 ng/L (Hg) working standard are added to the matrix reagents and brought to a final volume of 40 mL with ultra-pure mercury-free deionized water. Calibration curve concentrations range from 1 to 100 ng/L. Certified reference material BCR-679, White Cabbage, is certified at 6.3 µg/kg with an uncertainty of ±1.4 µg/kg. In solution 0.1g of sample has an expected mercury concentration of approximately 15.75 ng/L. The certified data is collected from the un-weighted mean value of the means of 8 accepted sets of data and corresponds to a level of confidence of 95%.

Conditions

Gas Flow (ml/min)	40
Pump speed (%)	100
Sipper depth (mm)	128
Sample uptake time (s)	60
Rinse time (s)	140
Read delay time (s)	71
Replicate read time (s)	2
Replicates	4
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Profile Replicate %RSD	0%

Figure 2. Method Parameters

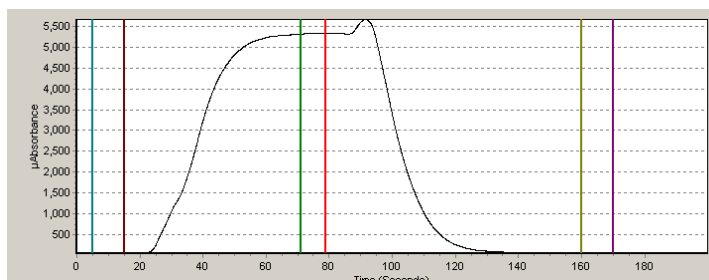


Figure 3. Standard Peak Integration

CALIBRATION STANDARDIZATION

Calibration standards are prepared with the appropriate aliquots of a 200 ng/L working standard. The working standard is prepared from dilutions of a 1000 mg/L certified mercury standard. Each calibration standard is brought up to a final volume of 40 mL. Aliquot volumes of 0.2 mL, 1.0 mL, 2.0 mL, 5.0 mL, 10.0 mL, and 20 mL are added to 2 mL of ultra-pure mercury-free deionized water, and 3 mL of aqua regia deionized water is added to give a final volume of 40 mL. The calibration standards were 1, 5, 10, 25, 50, and 100 ng/L respectively. The calibration is analyzed starting with the calibration blank and then proceeds from lowest to highest mercury standard. Each standard peak is integrated for a total integration time of 8 seconds. The mean concentration and the R^2 value are calculated and recorded.

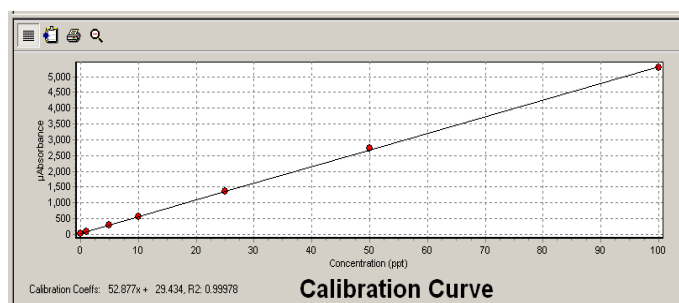


Figure 4. Method Calibration

PROCEDURE

Certified reference material BCR-679, White Cabbage, is digested and analyzed for total mercury quantitation using the QuickTrace™ M-7500. The standard reference material is shaken for approximately five minutes in order to re-homogenize the sample. A 50 mL polystyrene beaker is pre-cleaned and the sample is gently tapped into a pre-cleaned polystyrene beaker to minimize contamination of the stock sample source. Approximately 0.1g of the reference material is weighed out into a tarred pre-cleaned 50 mL polypropylene digestion tube. A 3.0 mL aliquot of aqua regia is added directly to the sample. The digestion vessel is capped and mixed thoroughly to ensure that the cabbage is in solution and the sample is digested at ambient temperature overnight. After digestion 37 mL of ultra-pure mercury-free deionized water is added to the sample to give a final volume of 40 mL. The digestion vials are placed directly on the autosampler rack for analysis. Inorganic mercury is reduced to elemental mercury by excess online addition of 10% stannous chloride in 7% hydrochloric acid at a rate of 3.8 mL/min at 100% pump speed. Sample uptake is 60s, sample volume is ~9.3 mL. Each sample peak is integrated for a total of 8 seconds. The %RSD is calculated based on the standard deviation and mean concentration. Initial calibration verification, initial calibration blank, quality control spike, matrix spike, and matrix spike duplicate are analyzed for instrument validation. The initial calibration verification is prepared by adding 5 mL of 200 ppt working standard into 32 mL ultra-pure mercury-free deionized water and 3 mL of aqua regia into a 50 mL polypropylene centrifuge tube for a concentration of 25 ng/L. The matrix spike and matrix spike duplicate are spiked pre-digest with 2 mL aliquots of 200 ng/L working standard and the quality control spike is spiked post-digest with 2 mL aliquot of 200 ng/L working standard for a concentration of 10 ng/L. Both spikes are added to 3 mL aqua regia in a 50 mL polypropylene centrifuge tube, then brought up to volume with 35 mL ultra-pure mercury-free deionized water. Calibration standards, samples, and quality controls are all matrix-matched to minimize biased results.

RESULTS

Total mercury in White Cabbage is easily recovered and quantified by optimizing instrument parameters in the QuickTrace™ software. Seven replicates of the certified reference material are analyzed and the total mercury concentration is recorded from peak integration. The results of $5.6 \mu\text{g}/\text{kg} \pm 1.7$ are shown in figures 5 and 6. Uncertainty values are calculated based on standard deviation and mean concentration and compared to the known values of the certified reference material. The certified mean mercury concentration for BCR-679 is $6.3 \mu\text{g}/\text{kg}$ with an uncertainty value of $\pm 1.4 \mu\text{g}/\text{kg}$. Uncertainty values for both the certified concentration and the measured concentration are based on seven replicates and calculated on a 95% confidence level.

Cabbage, BCR-679, $6.3 \mu\text{g}/\text{kg} \pm 1.4$		
Digest	$\mu\text{g}/\text{kg}$	
1	7.5	
2	5.0	
3	5.2	
4	5.4	
5	5.3	
6	5.6	
7	4.9	
Mean =	5.6	
Uncertainty =	1.7	
n = 7 Replicates	STD = 0.8886	RSD% = 15.989

Figure 5. Dilution Corrected Results

Using the QuickTrace™ M-7500 for measurement of low-level mercury is an effective analytical technique used for obtaining reliable quantitative data. Optimizing carrier gas flow, pump speed, sample uptake and rinse time allows for analysis of a calibration, quality controls, and samples over a broad dynamic range. Minimal sample analysis time reduces laboratory costs, analyst time and effort along with minimizing instrument maintenance, while giving reliable, quantitative data.

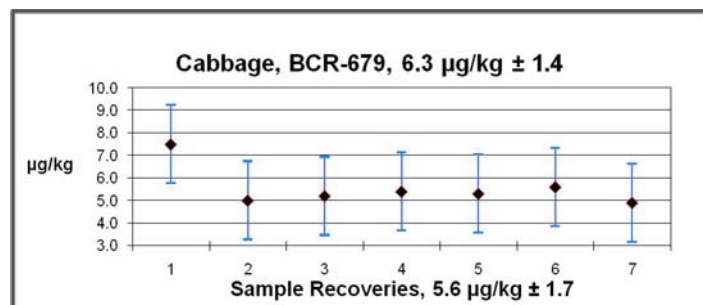


Figure 6. Dilution Corrected Results with Uncertainties

REFERENCES

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