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Application Note

Mercury Determination in Rice Flour, SRM 1568a, using the CETAC QuickTrace™ M-8000 CVAFS

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INTRODUCTION

Total mercury measurement in foodstuffs is an important analytical tool. Mercury bioaccumulation can occur in through various ways, and can include either absorption of mercury through the plant leaves from the atmosphere or from the soil and into the root system. Mercury contamination in the soil can come from agricultural land, municipal sludge and industrial wastes. The goal of this application note is to validate the QuickTrace™ Mercury Analyzer M-8000 Cold Vapor Atomic Fluorescence analyzer in the low ppt concentration range using non-amalgamation mode. Analysis is carried out by quantifying total mercury in the standard reference material 1568a, Rice Flour. A modified method was developed to carry-out this specific application.

INSTRUMENTATION

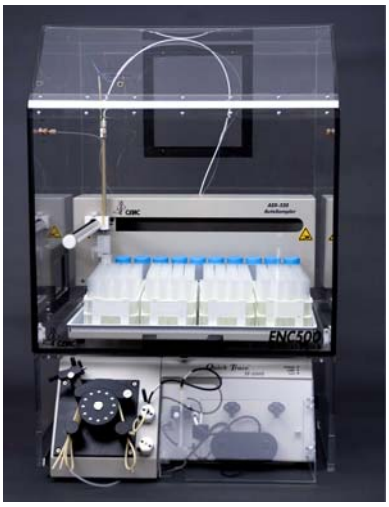

Figure 1. QuickTrace™ M-8000 Mercury Analyzer

The QuickTrace™ M-8000 is a stand-alone independent cold-vapor atomic fluorescence spectrometer for mercury analysis in all different sample types. The QuickTrace™ M-8000 is used for quantitative analysis of total mercury within a large working range. The QuickTrace™ M-8000 is accompanied with an autosampler and allows for hands free sample-batch analysis. A twelve roller four-channel peristaltic pump guarantees smooth sample delivery into the sample cell along with online sample reduction of inorganic mercury to elemental mercury. The reduced sample is pumped over the gas-liquid separator where the sample is liberated from the liquid and is carried by the carrier gas into the system. The sample is detected by a photomultiplier tube 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. Optimizing various instrument parameters results in total mercury analysis throughout a broad range.

EXPERIMENTAL

The QuickTrace™ M-8000 instrument detection limit is < 0.05 ppt and can be extended to > 400 ppb. Minimal instrument drift guarantees long-term stability for larger sample batch analysis. This specific application is developed for the quantification of mercury in the low ppt range with analysis of SRM 1568a, Rice Flour. Rice Flour is digested using mercury-free concentrated nitric, sulfuric and hydrochloric acids, and digested on a hot block at approximately 95 °C for 2 hours. The carrier gas is set at approximately 35 psi with instrumental flow set to low which yields approximately 65 mL/min through the system. The standard reference material 1568a, Rice Flour, is stored in a 500g glass jar. The sample is shaken for approximately five minutes prior to sample analysis to ensure sample homogeneity. Each sample is digested and analyzed in pre-cleaned 50 mL polypropylene centrifuge tubes. The tubes are cleaned with dilute detergent, 30% HNO_3, and three ultra-pure mercury-free deionized water rinses. Liberated inorganic mercury is reduced with the excess online addition of stannous chloride. 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.

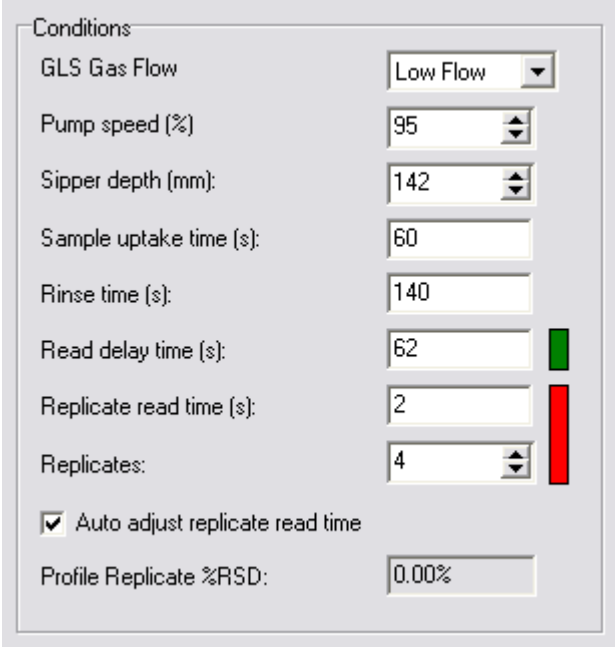

Figure 2. Method Parameters.

A normal linear calibration is analyzed and includes five 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 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 50 ng/L. Certified reference material 1568a, Rice Flour, is certified at 0.0058 mg/kg with an uncertainty of ± 0.0005 mg/kg. In solution 0.05g of sample has an expected mercury concentration of approximately 7 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%.

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. Aliquot volumes of 0.2 mL, 1.0 mL, 2.0 mL, 5.0 mL and 10.0 mL are added to 1mL concentrated nitric acid, 0.5 mL concentrated sulfuric acid and 3 mL of concentrated hydrochloric acid, each calibration standard is brought up to a final volume of 40 mL with 3% hydrochloric acid to give calibration standards of 1, 5, 10, 25 and 50 ng/L respectively.

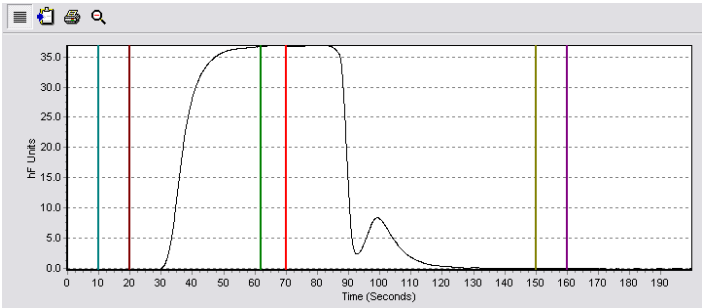

Figure 3. High Standard Peak Profile

The calibration is analyzed starting with the calibration blank and then proceeds from lowest to highest mercury standard. Each peak is integrated for eight seconds. The R^2 are calculated and recorded.

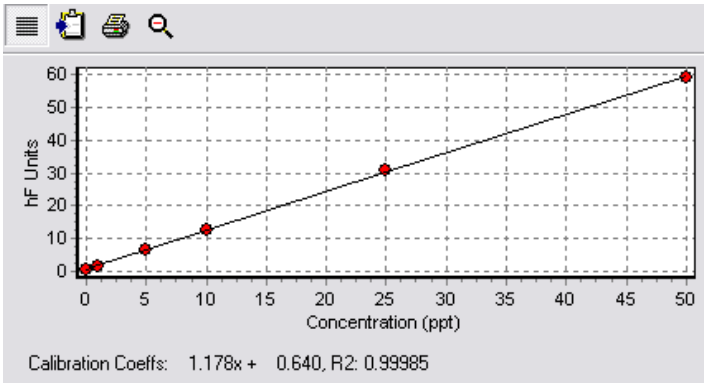

Figure 4. Calibration

PROCEDURE

Standard Reference Material 1568a, Rice Flour, is digested and analyzed for quantitation of total mercury using the QuickTrace™ M-8000. 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 with 10% nitric acid and rinsed three times with mercury-free deionized water. The sample is gently tapped into the beaker to minimize contamination of the stock sample source. Approximately 0.05g of the reference material is weighed out into tarred pre-cleaned 50 mL polypropylene digestion tubes. To these tubes 1.0 mL of concentrated nitric acid is added and the sample is allowed to sit for 15 minutes. This is repeated with 0.5 mL of concentrated sulfuric acid and 3.0 mL concentrated hydrochloric acid, separately. Finally, 20 mL of 3% hydrochloric acid is added and the samples are digested in a Fisher® hot block for two hours at 95 °C. When digestion is complete, the samples are cooled to ambient temperature and the walls of the digestion tube were rinsed with 3% hydrochloric acid and brought up to a finial volume of 40 mL. The digestion vessel is capped and mixed thoroughly to ensure that the sample is homogenized. 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 95% pump speed. Each sample peak is integrated for a total analysis time 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 2 mL of 200 ppt working standard into 1 mL concentrated nitric acid, 0.5 mL concentrated sulfuric acid and 3 mL of concentrated hydrochloric in pre-cleaned 50mL polypropylene tubes. To the calibration controls 3% hydrochloric acid is added to give a final volume of 40 mL for a concentration of 10 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 1 mL of concentrated nitric acid, 0.5 mL of concentrated sulfuric acid and 3 mL of concentrated hydrochloric acid. To the spike controls 3% hydrochloric acid is added to give a final volume of 40 mL for a concentration of 10 ng/L. Calibration standards, samples, and quality controls are all matrix-matched.

RESULTS

Total mercury in rice flour in the low ppt range 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 0.0060 mg/kg ± 0.0007 are shown in figures 5 and 6. Uncertainty values are calculated based on standard deviation and mean concentration and are compared to the known values of the certified reference material. The certified mean mercury concentration for SRM 1568a, Rice Flour is 0.0058 mg/kg,

with an uncertainty of ±0.0005 mg/kg. The measured concentration is based on seven replicates and calculated on a 95% confidence level.

NIST Mercury In Rice, SRM 1568a, 0.0058 mg/kg ± 0.0005			
Digest	**mg/kg**		
1	**0.0063**		
2	**0.0055**		
3	**0.0062**		
4	**0.0061**		
5	**0.0059**		
6	**0.0056**		
7	**0.0064**		
Mean =	**0.0060**		
Uncertainty =	**0.0007**		
n = 7 Replicates	**STD = 0.0003**	**RSD% = 5.774**	

Figure 5. Dilution Corrected Results

Using the QuickTrace™ M-8000 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.

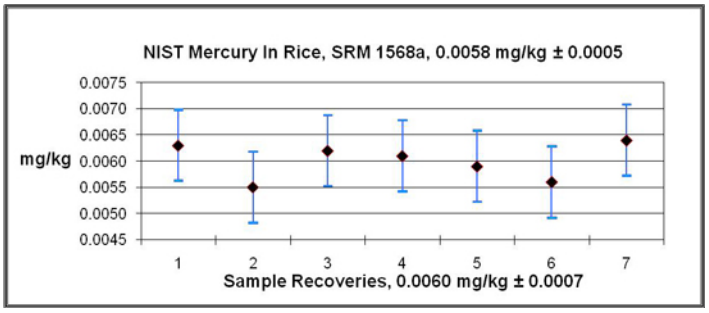

Figure 6. Dilution Corrected Results with Uncertainties

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