



Detection of total mercury in cotton matrix

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ABSTRACT

Cryogenic homogenized cotton samples were tested for mercury traces with very low concentrations we used analysis technique namely Cold Vapor/ Isotope Dilution ICP-MS. Target element is listed in Öko-Tex Standards and it should be absent or less than 0.02 mg/kg in the tested cotton samples for baby, direct skin contact and decoration products. Due to the presence of Hg in a very low concentration we need to measure it with high accuracy and low uncertainty sources testing method. In this work a previously homogenized Egyptian cotton samples were tested for total content of mercury. These samples included cotton varieties represent extra long staple (Giza 70 and 88) and long staple (Giza 89). The measurements were made using isotope dilution cold vapor inductively coupled plasma- mass spectrometry (ID-CV-ICP-MS) with Carius tube digestion. The results showed that the tested homogenized cotton samples have very low concentrations that cannot be detected by many other mercury analysis techniques. Uncertainty budgets also estimated in this work for all samples.

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Introduction

Mercury is a naturally occurring element. Mercury is mobilized from natural sources (such as volcanoes) and human activities (such as industrial combustion and mining) and mercury contamination is widespread in the United States and global environment. Human activities have increased the amount of mercury that is mobilized in the atmosphere; in soils and sediments; and in lakes, streams, and oceans (U.S. EPA, 2006, EPA's Roadmap for Mercury). Mercury can then be transported, depending on the form emitted and other factors, on local, regional and global scales before depositing in water. In aquatic ecosystems, mercury can be environmentally transformed into the organic form of mercury, methyl mercury, which can bioaccumulate and bio-magnify through food webs, and is highly toxic. Mercury exposure can cause a number of adverse effects on human health. These effects vary depending on the form of mercury to which a person is exposed and the level and length of exposure. The primary way humans are exposed to mercury is through eating fish containing methyl mercury. Methyl mercury exposure can cause neurological impairment, though research shows that most people's fish consumption does not cause a health concern. Fetuses and very young children are more sensitive to methyl mercury than adults [1].

Under normal cultivation, cotton [2] may be exposed to significant quantities of chemical contaminants, including herbicides, pesticides, defoliant and fertilizers. Additional chemicals may also be added during the manufacture of conventional cotton into clothing and other commercial goods. The measurement of some of these contaminants is becoming an important requirement. Although the levels of heavy metals in commercial grade cotton are believed to be low, there is interest in the measurement of trace elements and pollutants in Egyptian cotton and study their effects on the cotton quality. Mercury

should be not detected or less than 0.02 mg/kg [3-5] in cotton samples for skin contact and non skin contact, outwear and decoration textile products [6-9]. Many other heavy metals also interested e.g., Antimony, arsenic, cadmium, chromium, chromium IV, copper, cobalt and nickel [3].

Using a commercial atomic fluorescence instrument that employs an ICP as an atomization cell, a pulsed mercury hollow cathode lamp produced an unsatisfactory detection limit of only 0.5 mg l⁻¹. Consequently, the hollow cathode lamp was replaced with a mercury vapor lamp operating in the pulsed mode. Using this source and sample introduction by pneumatic cross flow nebulization, a detection limit of 0.03 mg L⁻¹ and an upper linearity limit of 300 mg l⁻¹ were achieved. For lower level mercury determinations, a continuous cold vapor generator was developed that interfaces with the instrument to leave the nebulizer intact. The generator allows mercury to be determined with a detection limit of 0.2 µg L⁻¹ while up to eleven other elements are simultaneously determined in the conventional manner. The cold vapor generator can also be used with the plasma off for single element mercury determinations. In this mode, a detection limit of 0.04 µg L⁻¹ was achieved [10]. Atomic absorption spectroscopy (AAS) and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) have been the EPA method of choice for the elemental analysis of soil extracts and aqueous samples because of their utility, sensitivity, and reliability. These methods can rapidly determine metals in trace amounts (after digestion) in many types of matrices [11]

The objective of this work was to measure accurately the levels of mercury in some Egyptian raw cotton varieties consisting of extra long staple (Giza 70 and 88) and long staple (Giza 89). The measurements were made using isotope dilution cold vapor inductively coupled plasma - mass spectrometry (ID-CV-ICP-MS) with Carius tube digestion, a method which has

been demonstrated previously [12,13] to provide concentration data of the highest accuracy on a variety of sample matrix types. These are the first known high accuracy determinations of mercury in cotton.

Experimental Work

Sample Identification

Three different samples of Egyptian cotton varieties namely Giza 70, Giza 88 and Giza 89 were supplied from Cotton Research Institute (CRI), Ministry of Agriculture- Giza, Egypt. Measurements on these materials were performed in triplicate. The samples were homogenized according in our previous work [14] according to cryogenic homogenization technique [15,16].

Sample Processing

Approximately 0.25 g of sample from each bottle was accurately weighed into a cleaned Carius tube via a transfer funnel, and spiked with an accurately weighed aliquot of ^{201}Hg , followed by the addition of 6 g of high-purity nitric acid. Each vessel was flame sealed, placed into a steel cylinder along with 20 g of solid CO_2 for external pressurization, and heated in a convection oven at 240 °C for twelve hours. After combustion with nitric acid a white flocculent precipitate was observed in all cotton samples. On dilution with high purity water, some of the precipitate was observed to dissolve or it may have just dispersed into fine particles. Future experiments will address the composition and decomposition of this phase. The head space of the Carius tubes containing the cotton samples was dark brown indicating that copious amounts of NO_2 were present. On venting the tubes it was observed that the pressure from CO_2 was considerably less than observed in other organic samples suggesting that the amount of carbon was less. After cooling to room temperature, each vessel was depressurized using a high temperature flame, and the contents transferred to 50 mL polypropylene centrifuge tubes. The contents were diluted to 15 mL with quartz-distilled water. The tubes were placed overnight in a refrigerator at 4 °C to allow degassing of excess nitrogen dioxide and carbon dioxide. Analytical measurements were completed within one day of dilution to reduce the risk of mercury losses from the solutions during storage and also external contamination by atmospheric mercury entering through the tube walls.

Cold Vapor / Inductively Coupled Plasma - Mass Spectrometry

Mercury measurements were made using cold vapor mercury generation coupled with ICP-MS isotope ratio measurements. The mercury vapor was generated using tin (II) chloride reductant (8% w/v in HCl) and separated from the liquid phase using a commercial (CETAC) glass reaction/separator cell. The vapor was transferred to a VG PQ2 ICP-MS system with 1/16" id Viton tubing, using an argon carrier gas flow rate of 100 mL/min. This gas stream was mixed with the plasma injector gas stream via a plastic T piece. The ICP was operated in a dry plasma mode, which necessitated slight re-tuning of the ion lenses relative to an aqueous aerosol sample introduction system. The ^{201}Hg and ^{202}Hg isotopes were monitored in a pulse counting Time-Resolved-Analysis mode (TRA) to recover the individual ion count rates. The isotope-time profiles were downloaded to a Microsoft Excel spreadsheet for calculation of background corrected $^{201}\text{Hg}/^{202}\text{Hg}$ ratios. Instrument mass discrimination was measured by generation of mercury vapor from an isotopic calibration standard. The discrimination factor was very close to unity during the period of measurement owing to the high mass of the isotopes and ion lens settings used. The instrument dead-time was determined using mercury vapor

generated from a standard (SRM 1641d) of natural isotopic composition.

Results and Discussions

Spike Calibration

The mercury levels in the cotton materials were anticipated to be quite low, and accordingly ^{201}Hg isotopic spike solution (of approximately 1 ng/g ^{201}Hg) was prepared by gravimetric dilution of an accurately calibrated master stock solution. The diluted spike was also separately calibrated by reverse isotope dilution using a high-purity primary standard (SRM 1641d). A stock solution was prepared by serial dilution of the primary standard which was then used to prepare two spike calibration mixtures. These were measured using cold-vapor ICP-MS. The overall mean measured concentration of the spike (n=2) was 5.8 pmol/g. The calibrated concentration of the spike was within 0.17 % of the value calculated from the gravimetric factors.

Samples

A summary of the results of the mercury concentration determinations in the three cotton materials are summarized in Tables 1, 2 and 3. The components of uncertainty are provided in Tables 4, 5 and 6 respectively. Type A uncertainty components were based on the variability of the sample measurements, the calibration of the working spike solution and the correction for the blank contribution. The uncertainty of the primary calibrant concentration, the weighing measurements, the ICP-MS instrument mass discrimination, correction for detector dead-time, and the subtraction of the instrument background were assessed as Type B uncertainty components. The uncertainties were combined according to ISO guidelines [17].

Isotopic Composition

As there are no commonly recognized spectral interferences for m/z 201 and m/z 202 and the isotopic composition of mercury has no natural variability, the isotopic composition of the material was not measured.

Blanks

Three total procedural blanks were run concurrently with samples. The average blank was 5.81 pg, which corresponded to a blank correction which ranged from 0.20% - 0.13% depending on sample size and concentration. The procedural blank data are summarized in Table 7. Blank correction data and sample size data are summarized in Table 8.

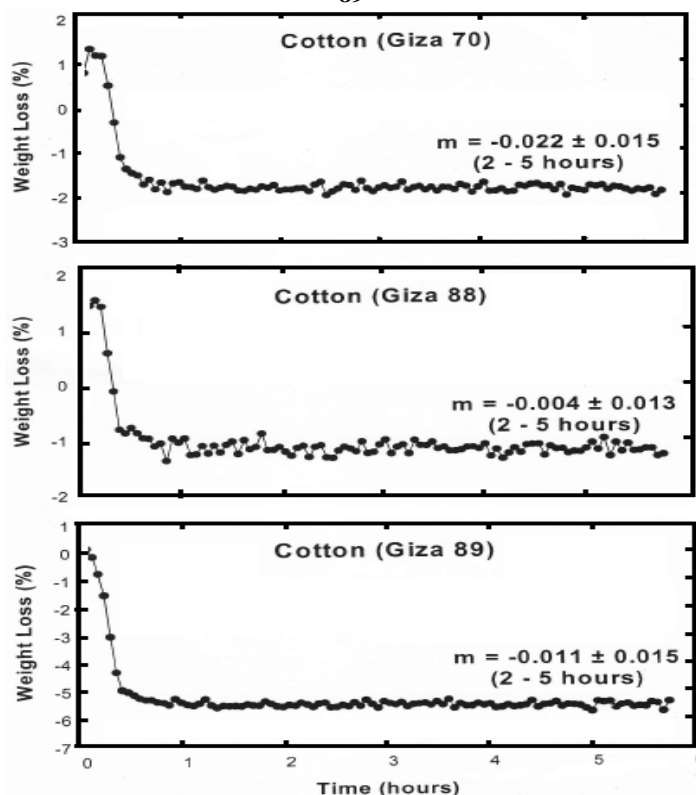
Correction for Moisture Content

The measured concentrations of mercury in the reference materials were corrected upwards to a dry mass basis by applying moisture analysis correction factors to each individual sample. These were determined by drying separate 0.5 g samples under dry high-purity nitrogen gas at 107 °C using the first NIST protocol [18], using a LECO TGA-501 gravimetric analyzer. The moisture loss correction factors are summarized in Table 9. Graphs showing the weight loss as a function of time are shown in Figure 1.

Conclusion

The results of Hg determination in the three homogenized Egyptian cotton varieties namely Giza 70, 88 and 89 and their expanded uncertainty (calculated with coverage factor equals 1.99 for Giza 70, 2.57 for Giza 88 and 3.18 for Giza 89 to give confidence level of 95%) were as follow:

Cotton Variety	Hg Concentration (ng/g)	Uncertainty (± %)
Giza 70	9.3	± 0.084
Giza 88	3.8	± 0.083
Giza 89	3.5	± 0.128

Figure 1: Weight Loss Graphs for Giza 70, Giza 88 and Giza 89**Acknowledgment**

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Table 1. Summary of results for Mercury in Giza 70 cotton

Giza 70	Hg (ng/g)
Replicate 1	9.312
Replicate 2	9.320
Replicate 3	9.284
Recommended value	9.305
Standard Deviation	± 0.0186
% RSD	0.199
Uncertainties	
Type A	± 0.0188
Type B	± 0.0377
Combined Uncertainty	± 0.0421
Coverage Factor	1.99
Expanded Uncertainty (95% Confidence Level)	± 0.084

Table 2. Summary of results for Mercury in Giza 88 cotton

Giza 88	Hg (ng/g)
Replicate 1	3.791
Replicate 2	3.862
Replicate 3	3.784
Recommended value	3.812
Standard Deviation	± 0.0432
% RSD	1.134
Uncertainties	
Type A	± 0.0274
Type B	± 0.0171
Combined Uncertainty	± 0.0323
Coverage Factor	2.57
Expanded Uncertainty (95% Confidence Level)	± 0.083

Table 2. Summary of results for Mercury in Giza 89 cotton

Giza 89	Hg (ng/g)
Replicate 1	3.598
Replicate 2	3.488
Replicate 3	3.496
Recommended value	3.527
Standard Deviation	± 0.0613
% RSD	1.737
Uncertainties	
Type A	± 0.0369
Type B	± 0.0158
Combined Uncertainty	± 0.0402
Coverage Factor	3.18
Expanded Uncertainty (95% Confidence Level)	± 0.128

Table 4. Components of Uncertainty for Mercury in Giza 70 cotton**Type A**

Source	Ci	Units	Ui	Units	C _i U _i	DF
Sample Measurement	1	--	0.01072	ng/g	0.01072	2
Spike Calibration	1	--	0.01369	ng/g	0.01369	1
Blank Correction	1	--	0.00718	ng/g	0.00718	2
Combined Type A Uncertainty					0.01881	2.908

Type B

Source	Ci	Units	Ui	Units	C _i U _i	DF
Primary Calibrant	1	--	0.01861	ng/g	0.01861	infinite
ICP-MS Discrimination Correction	1	--	0.01861	ng/g	0.01861	Infinite
ICP-MS Dead Time Correction	1	--	0.02326	ng/g	0.2326	Infinite
ICP-MS Instrument Background	1	--	0.01002	ng/g	0.01002	Infinite
Weighing Measurements	1	--	0.00931	ng/g	0.00931	Infinite
Combined Type B Uncertainty					0.03770	

Effective freedom – 73.13

Where Ci = correlation index, Ui = individual uncertainty source, DF is the degree of freedom.

Table 5. Components of Uncertainty for Mercury in Giza 88 cotton**Type A**

Source	Ci	Units	Ui	Units	C _i U _i	DF
Sample Measurement	1	--	0.02497	ng/g	0.02497	2
Spike Calibration	1	--	0.00561	ng/g	0.00561	1
Blank Correction	1	--	0.00975	ng/g	0.00975	2
Combined Type A Uncertainty					0.02739	2.814

Type B

Source	Ci	Units	Ui	Units	C _i U _i	DF
Primary Calibrant	1	--	0.00762	ng/g	0.00762	Infinite
ICP-MS Discrimination Correction	1	--	0.00762	ng/g	0.00762	Infinite
ICP-MS Dead Time Correction	1	--	0.00953	ng/g	0.00953	Infinite
ICP-MS Instrument Background	1	--	0.00831	ng/g	0.00831	Infinite
Weighing Measurements	1	--	0.00381	ng/g	0.00381	Infinite
Combined Type B Uncertainty					0.01705	

Effective freedom – 73.13

Where Ci = correlation index, Ui = individual uncertainty source, DF is the degree of freedom.

Table 6. Components of Uncertainty for Mercury in Giza 89 cotton

Type A						
Source	C _i	Units	U _i	Units	C _i U _i	DF
Sample Measurement	1	--	0.03538	ng/g	0.03538	2
Spike Calibration	1	--	0.00519	ng/g	0.00519	1
Blank Correction	1	--	0.00924	ng/g	0.00924	2
Combined Type A Uncertainty					0.03693	2.362

Type B						
Source	C _i	Units	U _i	Units	C _i U _i	DF
Primary Calibrant	1	--	0.00705	ng/g	0.00705	infinite
ICP-MS Discrimination Correction	1	--	0.00705	ng/g	0.00705	Infinite
ICP-MS Dead Time Correction	1	--	0.00882	ng/g	0.00882	Infinite
ICP-MS Instrument Background	1	--	0.00781	ng/g	0.00781	Infinite
Weighing Measurements	1	--	0.00353	ng/g	0.00353	Infinite
Combined Type B Uncertainty					0.01584	

Effective freedom – 3.18

Where C_i = correlation index, U_i = individual uncertainty source, DF is the degree of freedom.

Table 7. Process plank data for Giza 89, Giza 88 and Giza 89 cotton varieties

Giza 89	Hg (pg)	Hg (fmol)
Blank Replicate 1	9.82	48.9
Blank Replicate 2	2.66	13.3
Blank Replicate 3	4.95	24.7
Mean Blank	5.81	2.90
Standard Deviation	± 3.65	± 1.82
% RSD	62.9	62.9

Table 8. Sample size and Blank correction data for Giza 70, Giza 88 and Giza 89 cotton

Cotton Variety	Replicate Number	Mass Sample (g)	Blank Correction (%)
Giza 70	1	0.32381	0.20
	2	0.25770	0.25
	3	0.29907	0.21
Giza 88	1	0.23079	0.67
	2	0.23511	0.64
	3	0.21901	0.70
Giza 89	1	0.23260	0.73
	2	0.26080	0.67
	3	0.24068	0.72

Table 9. Weight loss data for Giza 70, Giza 88 and Giza 89 cotton materials

Cotton Variety	Replicate Number	Weight Loss (%)	Mean Weight Loss (%)
Giza 70	1	1.851	1.810
	2	1.750	
	3	1.829	
Giza 88	1	1.140	1.154
	2	1.211	
	3	1.110	
Giza 89	1	5.229	5.272
	2	5.509	
	3	5.077	