Determination of Mercury in Microwave Digests of Foodstuffs by ICP-MS

Application

Food Safety

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Abstract

The quantitative determination of mercury in foodstuffs is presented using a 7500i ICP-MS. Microwave digests were prepared and then analyzed by ICP-MS. To avoid memory effects often experienced with mercury, gold was added offline to all standards/samples and wash solutions to act as a cleansing agent. The instrumental setup used a second vacuum pump, the integrated sample introduction system in the high sample throughput mode, and a micro-flow concentric nebulizer. This allowed the robust and rapid determination of mercury in the digests at the ppt range. Excellent agreement with the certified value was obtained for two certified reference materials and stability of the system was demonstrated over a 36-hour analytical run.

Introduction

The determination of sub-ppb concentrations of mercury has always been of special importance in the field of trace metal analysis. Even at trace levels, mercury is toxic and causes neurological damage, particularly in fetuses and young children. Anthropogenic sources of mercury in the environment include coal-fired power stations and chlor-alkali works. In the aquatic environment, bacteria convert elemental mercury Hg(0) to methylmercury which is accumulated and passed up the food chain. It has been reported that some whale meat contains 5000 times the Japanese legal limit of 0.4 µg/g. In addition, fish and shellfish are significant contributors to the human diet. Today mercury pollution is a global problem and extensive monitoring of foodstuffs is required. Therefore fast efficient and robust methods are needed. Mercury however is recognized as a problem element. It is known to adsorb onto the walls of storage containers and volatilize as mercury vapor. Additionally, its high first ionization potential and numerous isotopes have limited its sensitivity in ICP-MS analysis. ICP-MS allows the rapid determination of ultratrace levels of metals in food digests, however, extensive washout times have been required to reduce carryover for mercury analysis. Other workers have tried the addition of a number of chemical agents in the past. One of the most effective washout agents is gold chloride. To avoid memory effects and ensure stability, gold chloride (at the 5-ppm level) was added offline to all samples/standards and wash solutions. Extensive washout times were reduced by using by the integrated sample introduction system (ISIS). With the use of the high throughput pump, a large flush volume can be pumped through in a much shorter time. By summing the responses for multiple isotopes (199, 200, 201, and 202) and with the help of a second interface vacuum pump and a micro-flow concentric nebulizer, detection levels of between 10 and 30 ppt were routinely achieved for the digests.

Procedure

Microwave Digestion

Varying aliquots of each sample (generally between 0.2 and 0.6 g, depending on the moisture content of the sample) were weighed to the nearest 0.01 g into the digestion vessels. Wet oxidation was induced using concentrated, ultra-high purity nitric acid (10 mL, from Romil LTD, Cambridge, UK) with the addition of a 0.2 mL of concentrated hydrochloric acid (Romil LTD, Cambridge, UK). Oxidation was carried out in heavy-duty vessels (HDV) using a high-pressure microwave digestion oven (Mars 5 from CEM). Temperature control was used as opposed to pressure control. Samples were ramped to 180 °C over 20 minutes and held at 180 °C for 10 minutes before cooling to below 50 °C before venting the vessel. Both pressure and temperature were monitored by direct measurement throughout the digestion to ensure that samples attained the critical temperature of 180 °C, at which food components, such as fat, are digested. The sample digests were then made up to 100 g using ultra-high purity water (18 mega ohms, from Elga Maxima). The resultant solution was used for determination.

Operating and Acquisition Parameters

Ten milliliter portions of the sample digests were accurately pipetted into sample tubes, and using a micropipette, 20 µL of a 1000-ppm gold chloride solution (Romil LTD, Cambridge, UK) was added. This gives a final gold concentration of 5 ppm in solution. Fifty milliliters each, of blank and four standard solutions covering the range, were prepared from a 100 µg/g stock mercury solution (from SPEX CertiPrep Assurance, Metuchen, New Jersey, USA). Ten percent wt/wt nitric acid containing 5 ppm of gold was used as the wash solution for the autosampler and nebulizer. Gold is thought to have its effect by acting as an oxidizing agent ensuring that mercury stays in an ionized form in solution. Gold was added at elevated levels to ensure that any residual amounts of organic compounds in the digests would not reduce Au(III) to elemental gold and render it ineffective. A 250-ppb Thalium standard was added online as an internal standard (ISTD), using the ISIS system. There was an online dilution factor of 1:20. Gold chloride was also added to the standard solutions at 5 ppm.

Instrument Conditions

Plasma gas flow rate	16 L/min
Carrier gas flow rate	0.85 L/min
Make-up flow	0.14 L/min
RF Power	1400 Watts
Nebulizer	Agilent micro-flow 100 µL
Spray chamber	Glass double pass
Spray chamber temperature	Cooled to 2 °C
ICP Torch injector	2.4 mm
Sample tubing	0.89 mm id
Internal standard tubing	0.19 mm id
Instrument Peri pump	0.1 rps
Sample/Skimmer cones	Nickel
Rotary pumps	2
Autosampler	AX500

Acquisition Parameters

Mass	Element	Integration/Point	Time (s)/Mass
199–201	Hg	3.5	10.5
202	Hg	3.5	10.5
205	Tl	0.05	0.15

Number of points per mass:	3
Acquisition time:	43.79 s
Number of repetitions:	3
Total acquisition time:	131 s

Peristaltic Pump Program

Memory effects arise when the analyte signal is enhanced due to contributions from previous high concentration sample. This is due to adsorption/desorption of mercury in the sample introduction system. As a result, the analyst has to program long washout times. With the use of ISIS this wash-out time can be reduced.

ISIS Peristaltic Pump Program

Analysis Speed : 0.10 rps

Before acquisition	
Uptake speed	0.80 rps
Uptake time	32 s
Stabilization time (undiluted)	150 s
After acquisition (probe rinse)	
Rinse speed	0.80 rps
Rinse time (sample)	8 s
Rinse time (standard)	8 s
After acquisition (rinse)	
Rinse vial	1
Uptake speed	0.8 rps
Uptake time (undiluted)	32 s
Stabilization time	85 s

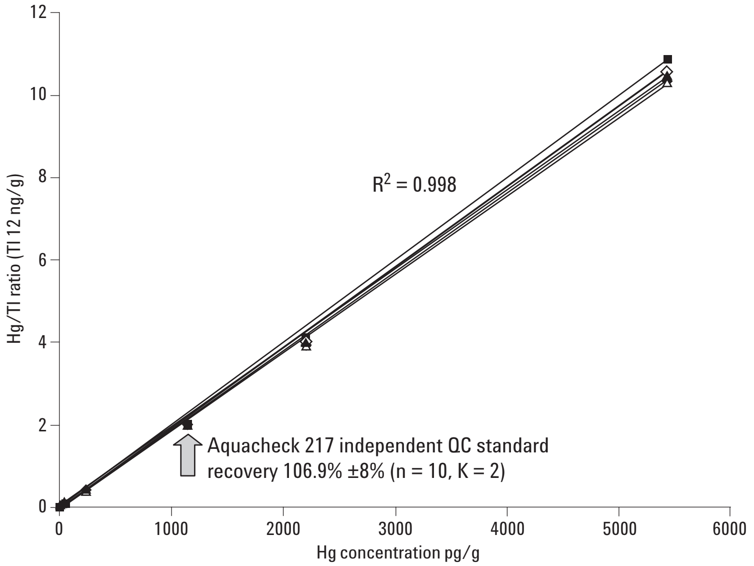


Figure 1. Calibrations over 36 hours continuous operation.

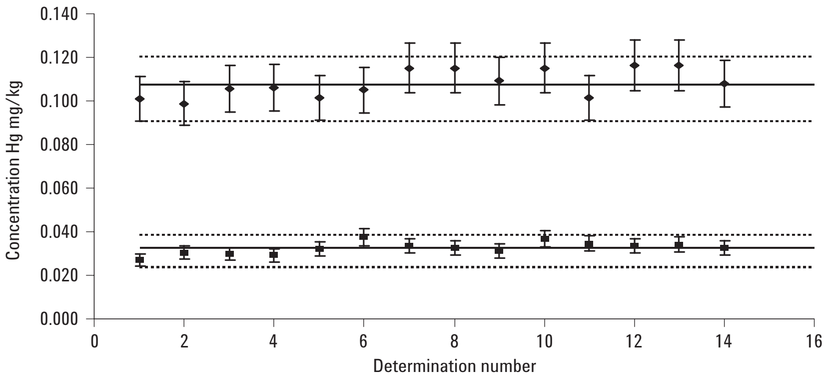
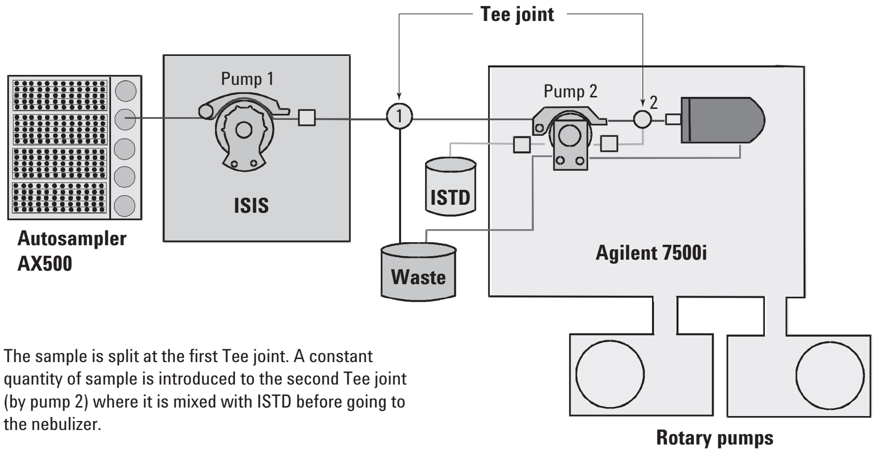


Figure 2. NIST 1547 Peach leaves (bottom trace) and LGC 7160 Crab paste (top trace) were analyzed 14 times over a period of 1 month. Each point represents a separate digest. LGC 7160 certified value 0.096 = ±0.108 mg/kg, NIST 1547 certified value 0.031 = ±0.007 mg/kg.



The sample is split at the first Tee joint. A constant quantity of sample is introduced to the second Tee joint (by pump 2) where it is mixed with ISTD before going to the nebulizer.

When going to the next sample the ISIS pump (pump 1) turns at high speed to shorten the sample and washout transfer times.

Figure 3. Schematic of ISIS in high sample throughput mode.

Results

Five calibration plots over a 36-hour period are shown in Figure 1 demonstrating excellent stability of the system. As can be seen, excellent linearity was achieved over an extended calibration range demonstrating that memory effects had been effectively eliminated. Between the calibrations over 120 various microwave foodstuff digests were analyzed.

Quality Control

An Aquacheck proficiency testing material solution from the Water Research Council (1010 ppt) was analyzed 10 times during the run and a mean recovery of 106.9% (±8%) was achieved (Figure 1). This material was analyzed throughout a run of 120 various foodstuffs samples and acted as a quality control for the quantitation.

Two certified reference materials (CRMs) were analyzed throughout a survey of 500 samples. These acted as quality control materials for the microwave digestion as well as the quantitation. The CRMs used were a crab paste—Metals LGC 7160, 0.096 mg/kg—and peach leaves—NIST 1547, 0.031 mg/kg. Each CRM was analyzed 14 times on different runs during a survey of more that 500 samples of various foodstuffs over a 1-month period. The results can be seen in Figure 2.

Conclusion

This procedure proved robust, as in excess of 500 samples were analyzed in runs lasting in excess of 36 hours without loss of sensitivity.

The 7500i ICP-MS has shown to be a robust and sensitive tool for the analysis of foodstuff for mercury. The system proved stable over an extended time period. The use of the ISIS enables the operator to take advantage of the high sample throughput possible with this technique. The use of Au(III), in particular, shortens washout time considerably, reducing the possibility of carry-over. The sensitivity of the 7500i ICP-MS gives method detection limits at low ppt levels in the foodstuff digests. The extended calibration range reduces the need for dilutions and reruns.

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