

### Challenge

Meeting new industry regulations for mercury (Hg) in environmental waters

### Solution

PlasmaQuant® MS with high-throughput sample introduction system and sub ng/L detection limit for mercury (Hg)

## Ultra-trace Determination of Mercury in Environmental Waters Using the PlasmaQuant® MS

### Introduction

Mercury is a well-known toxic element and considered as one of the top ten chemicals of public health concern by the World Health Organization. It is a neurotoxin that rapidly bioaccumulates and can cause major health problems, and even death, in small quantities. Chronic exposure at low levels is known to affect the nervous, digestive and immune systems as well as the lungs, kidneys and eyes with fetuses and breast feeding babies susceptible to developmental effects.

Mercury is a naturally occurring element found in air, water and soil through volcanic activity. Although, human activity contributes significantly through the burning of coal, waste incineration, mining and other industrial uses, finding its way into the environment and eventually, into the food chain. It exists in various forms including the elemental or metallic form, the inorganic form as in mercury salts, and the organic form with methylmercury being the most toxic.

The determination of mercury concentrations in environmental samples such as natural waters and waste waters is important in environmental risk assessment. On the 23<sup>rd</sup> of October 2000, the "Directive 2000/60/EC of the European Parliament and of the Council establishing a framework for the Community action in the field of water policy" or, in short, the EU Water Framework Directive was formerly adopted. Mercury and its compounds are part of this directive. Environmental quality standards (EQS) of 2008/105/EC define the maximum allowable concentration (MAC) for mercury as 0.05 µg/L.

Recent regulations set the limits of quantification for mercury in environmental waters. These limits are detailed in table 1.

Table 1: Limits of quantification relative to Hg

Code	Name	Matrix	Limit of quantification	Effective date
1387	Mercury	Fresh water	0.050 µg/L	Prior to the 15th of July 2013
1387	Mercury	Fresh water	0.015 µg/L	From the 15th of July 2013
1387	Mercury	Waste water	0.5 µg/l	From the 15th of July 2013

### Instrumentation

- PlasmaQuant® MS: Inductively Coupled Plasma – Mass Spectrometer
- ASPQ 3300 autosampler
- ESI oneFAST high-throughput sample introduction system

### Method

The system was optimized for lowest detection limits of mercury and minimum oxide formation. A solution of 1 µg/L Hg was used to optimize the ion optics for maximum signal for Hg isotopes listed in table 2. The sum of the four Hg isotope masses were used for calculations, allowing a higher signal to be recorded for improved precision and detection limits. Given there is the potential for Hg isotopes to be interfered with by the formation of tungsten oxides (WO<sup>+</sup>) polyatomics, the plasma conditions were set for minimum oxide formation at <2 % (CeO to Ce ratio). The instrument parameters are listed in table 2.

Table 2: Instrument parameters

Parameter	Specification
Plasma Gas	9.0 L/min
Auxiliary Gas	1.25 L/min
Nebulization Gas	1.00 L/min
Sampling Depth	5.0 mm
RF power	1.4 kW
Pump rate	10 rpm
Measured Hg isotopes	198, 199, 200 and 202
Scan Mode	Peak hopping
Points per Peak	1
Scans per Replicate	30
Replicates	3
Dwell Time	50 ms
Rinse time	30 s

## Samples and Reagents

- High purity ICP-MS grade nitric acid (NORMATOM from VWR)
- High purity ICP-MS grade hydrochloric acid (NORMATOM from VWR)
- Potassium bromide (Merck)
- Potassium bromate (Merck)
- Hydroxylammonium chloride (Merck).
- Mono-elemental mercury stock standard solution (100 mg/L, Inorganic Ventures)
- National Research Council Canada ORMS-5 River Water (Certified Reference Material)
- LGC Stanards ERM-CA615 Ground water (Certified Reference Material)

## Sample and Standard Preparation

A combined step of conservation and digestion was carried out. Mono and organomercury compounds of Hg are converted into divalent mercury by oxidation using a mixture of potassium bromide and potassium bromate (KBr/KBrO<sub>3</sub>) in 1 % HCl. The excess of bromide is stabilized with hydroxyl ammonium chloride. Approximately 5.95 g of KBr (Merck) and 1.39 g of KBrO<sub>3</sub> (Merck) were dissolved in 500 ml deionized water. Both powders (KBr and KBrO<sub>3</sub>) were dried overnight at 300°C prior to dissolution to remove any traces of mercury contamination. The hydroxyl ammonium chloride (NH<sub>4</sub>ClOH) solution was prepared by dissolving 6 g in 50 ml of deionized water.

Solutions were prepared by adding 0.5 mL of 1 % HCl (v/v) and 1.0 mL of the above KBr/KBrO<sub>3</sub> solution into 50 mL of the standard and sample solutions. They were then left at room temperature for 15 minutes to allow the reaction to occur (solutions develop a yellow tint) after which 1.0 mL of NH<sub>4</sub>ClOH was added to neutralize the Br<sub>2</sub> formed and producing a clear solution.

Two certified water reference materials and three proficiency test water samples were prepared and analyzed. A mono-elemental mercury stock standard solution from Inorganic Ventures (100 mg/L) was used to make up all calibration solutions, covering the range from 10 ng/L up to 1000 ng/L (figure 1). <sup>193</sup>Ir was used as an internal standard to correct for any possible signal drift or matrix effect.

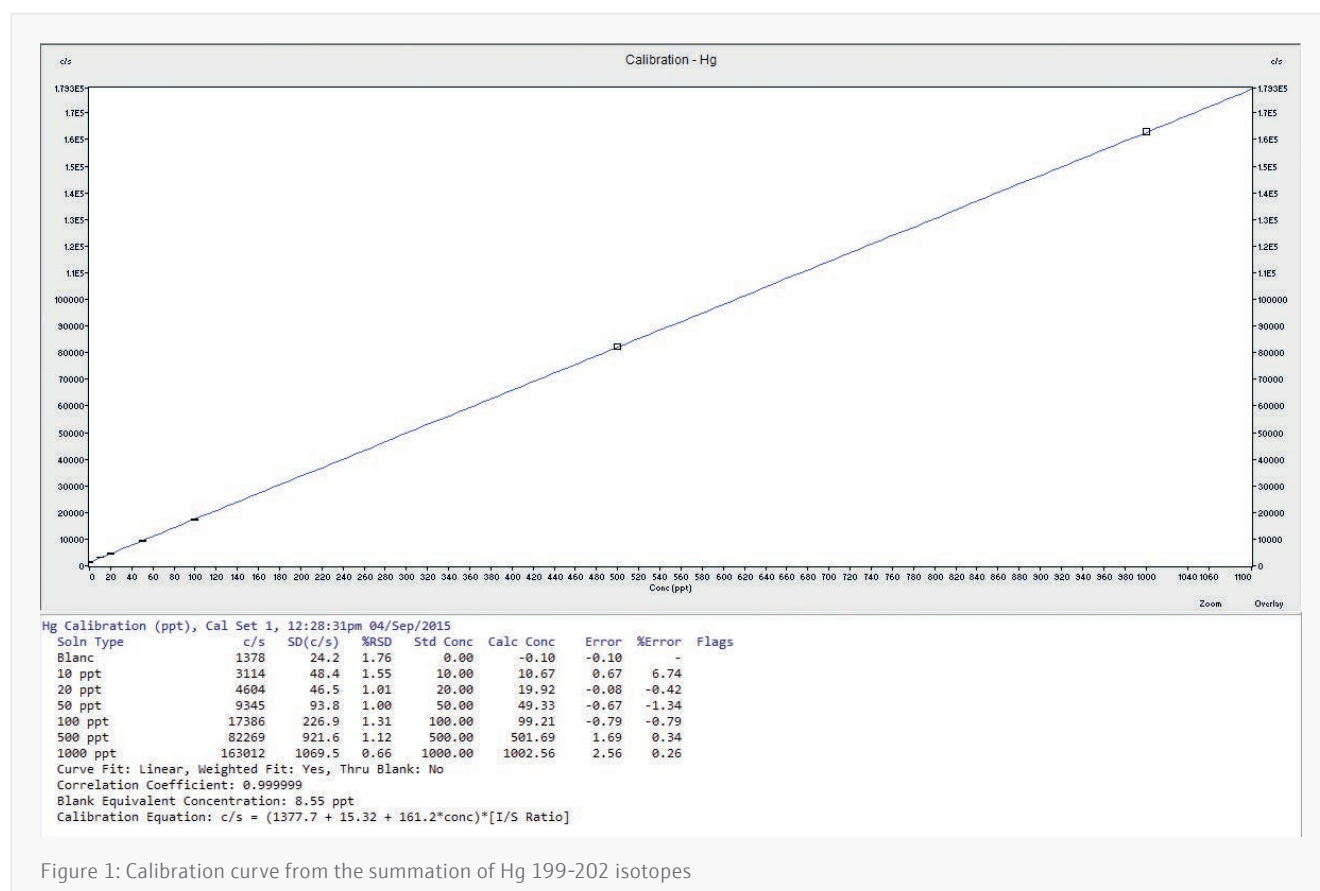


Figure 1: Calibration curve from the summation of Hg 199-202 isotopes

## Results and Discussion

The measured and certified values for Hg in river and ground water reference materials are shown in table 3.

The measured and expected values for natural, drinking and waste waters, along with the Z-score are reported in table 4. The Z-score indicates how many standard deviations the measured value is from the mean value and was determined to be  $\leq \pm 1$  for this analysis.

Table 3: Reference materials results

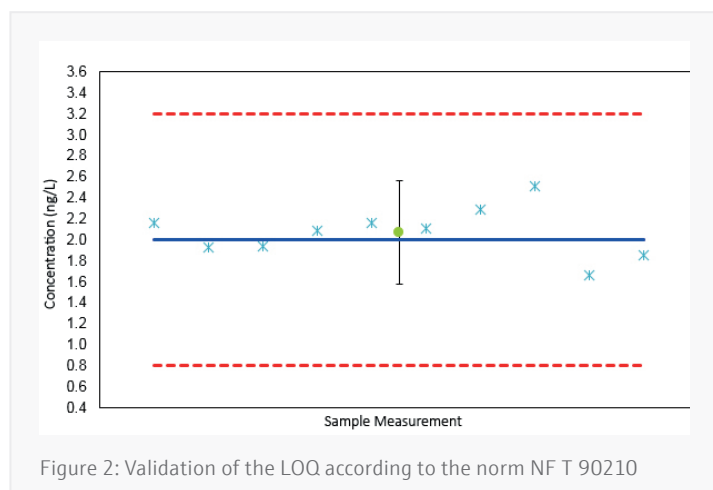
Reference material	Certified value (ng/L)	Measured value (ng/L)
ORMS-5 River water	37.0 ± 4.0	36.6 ± 0.8
ERM-CA615 Groundwater	26.2 ± 1.3	26.4 ± 0.8

Table 4: Proficiency tests results

Proficiency test	Measured value (µg/L)	Assigned value (µg/L)	Z-score
Natural water	1.2	1.1	0.3
Drinking water	2.7	2.5	1.0
Waste water	34.5	35.0	-0.1

Linearity tests, limit of quantification and accuracy profiles were evaluated according to the French norm NF T 90210 (2009). A natural water sample collected from a river in Vendée, France, was used to estimate the limit of quantification (LOQ). A final LOQ of 2 ng/L was determined along with a  $3\sigma$  method limit of detection (MDL) of 0.3 ng/L.

Figure 2 shows the readback of a 2 ng/L spiked water sample measured 10 times over the duration of 5 days. The readback at the LOQ was easily within the  $\pm 60\%$  concentration range as defined by the NF T 90210 norm.



### Sample introduction Washout Test

Mercury is known to exhibit serious memory effects, affecting data quality at ultra-trace concentrations. Sample preparation and instrument setup is important to minimize memory effects. A study was carried out to demonstrate the effectiveness of the sample preparation and the washout efficiency of the sample introduction system.

The oneFAST high throughput sample introduction system from Elemental Scientific is a software controlled, switching valve system that greatly improves the efficiency of sample uptake and washout. This includes reducing the volume of sample required for analysis and contact time with sample introduction tubing. A blank solution was routinely run immediately after the top standard (1000 ng/L) with washout to less than 1 ng/L achieved in under 30 seconds.

## Conclusion

The superior sensitivity of the PlasmaQuant® MS offers reliable ultra-trace determination of mercury in environmental waters. A method LOD of 0.3 ng/L was obtained without the need for pre-concentration techniques (e.g. hydride or cold vapor generation). The ASPQ 3300 autosampler with oneFAST sample introduction system ensures high efficiency and reduced memory effects. Results obtained on reference materials and proficiency tests were in excellent agreement with certified values and well within defined ranges. The modern RF generator design of the PlasmaQuant® MS Elite provides very robust plasma conditions for complex wastewater samples containing high total dissolved solids, and with only half the argon gas consumption.