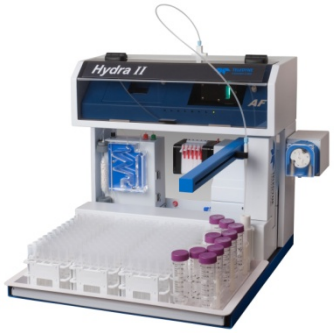
Quality Control Considerations for EN 17852 The Determination of Mercury Using Atomic Fluorescence Spectroscopy

Application Note #1302

Abstract



The European Norm EN17852 Water quality - Determination of mercury - Method using atomic fluorescence spectrometry (ISO 17852:2006) has many similarities to USEPA Method 245.7. (See Table 1) Both were designed to produce more accurate mercury results than cold vapor atomic absorption techniques at very low concentrations. In terms of the way the sample is handled and analyzed the two methods are quite similar but EN17852 does not include most of Method 245.7's embedded quality control. Many of the quality controls found in USEPA Method 245.7 can be found in Mcerts "Performance Standard for Organisations Undertaking Sampling and Chemical Testing of Water" (Section 5.6 Assuring the quality of test results). This presentation will identify similarities and significant differences between the two methods. In particular, we will look at USEPA Method 245.7 quality control requirements and the purpose of each quality control item. Additionally, results obtained using EN 17852 methodology will be presented.

Methods Overview

	En 17852	USEPA 245.7
Sample Pretreatment	Optional	Mandatory
Analytical Range	1-100 ng/L 10-100 ng/L[1]	5-100 ng/L
Calibration Standards	10, 30.50, 70, 100 ng/L (2, 5, 10, 15, 20 ng/L[2])	5, 10, 25, 50, 100 ng/L
Calibration Fit Type	Linear (Non Linear fits permitted)	Calibration Factor
Sample Type	Drinking, Surface, Ground, Rain Waters (Industrial Waste & Waste Water[3])	Drinking, Surface, Ground, Marine, Industrial and Municipal Wastes
Preservation	BrCl	5 mL/L HNO_3
Digestion	BrCl	BrCl
Pre-Reduction	L-ascorbic acid (Hydroxylamine hydrochloride)[4]	Hydroxylamine hydrochloride
Final Reduction	$SnCl_2$	$SnCl_2$
Contact Materials	Glass or special plastics e.g. FEP	Borosilicate glass or Teflon
Moisture Removal	Hydroscopic Membrane[5]	Nafion

Table 1: Comparison of method characteristics

[1] Often used as the practical range (section 1)

[2] Optional low range calibration (section 5.10.5)

[3] Allowed with modified sample pretreatment (Introduction)

[4] Optional (A.2 Annex)

[5] A chemical desiccant can be substituted (A.5 Annex)
Nafion membrane identified (C.3 Annex)

Instrumentation

As defined in both methods, samples and stannous chloride are pumped into a gas/liquid separator[6] where the liquid is removed to waste and the gaseous mercury is transported via a carrier gas bubbled through the solution to a fluorescence cell for detection. Figure 1 provides a simplified schematic diagram of the instrumentation requirement. For the data presented in this report the Hydra II_{AF} system from Teledyne Leeman Labs was employed. Table 2 shows the operating parameters for the system.

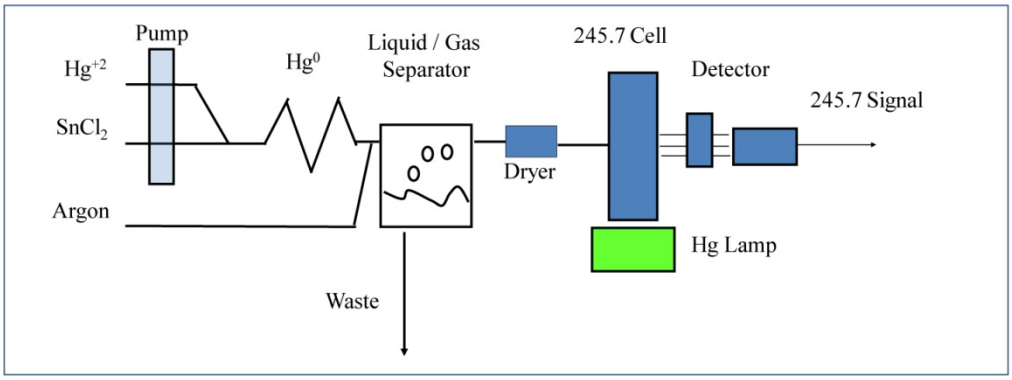


Figure 1: Schematic of Fluorescence system

[6] While Method 17852 specifies a gas/liquid separator in Section 9.1 and Annex B, some instruments are designed to perform the separation of gas and liquid phases in the sample cup itself.

Integration Time	5 sec
# of Replicates	2
Uptake Time	65 sec
Rinse Time	60 sec
Sample Pump Speed	10 mL/min
Carrier Gas Flow Rate	250 mL/min

Table 2: Operating Parameters

USEPA Calibration Factor

As stated in Table 1 USEPA Method 245.7 requires use of the Calibration Factor curve fit algorithm. This algorithm is a linear fit designed to provide better accuracy at lower concentrations. Basically, the signal for each non-zero standard is divided by its concentration to generate a slope for that point. The sample signal is then divided by the average slope of the standards to return a concentration. There are three requirements before any calibration can be used. First, blanks must be less than the method limit (ML) defined as 1.8 ng/L. Second, the relative standard deviation of all the calibration factors must be less than 15%. Third, The lowest non-zero standard must be within 75-125% of its designated concentration. In these data the blank is acceptable at 0.13 ng/L, the calibration factor %RSD is 4.6%, and the report limit recovery is 104%. Using the same calibration data Table 3 shows the improved accuracy at lower concentrations using the calibration Factor algorithm.

Standard Concentration ng/L	Mean Signal	Least Squares Linear Fit	Weighted Linear Fit	Calibration Factor Fit
0	170	-0.41	-0.09	0.13
1	1326	0.55	0.84	1.04
5	6811	5.11	5.28	5.33
10	12704	10.01	10.04	9.95
20	25376	20.55	20.28	19.87
50	61538	50.63	49.50	48.19
100	120354	99.56	97.02	94.25

Table 3: Comparison of calibration algorithms

Quality Control Requirements

Table 4 contains references to quality control requirements from the mCerts Performance Standard for Water (section 5.6.2 and USEPA Method 245.7 (sections 9.1-9.5). It should be noted that USEPA employs specific language that distinguishes between requirements and suggestions. Where "shall" or "must" items are mandated while "may" or "should" items are recommended. The mCERTs relies more on Interlaboratory comparisons (5.6.2) and recoveries for Certified Reference Materials (5.6.3.1) than does Method 245.7.

Control	245.7 Test	245.7 Requirement	mCERTs Test	mCERTs Requirement
Detection Limit	MDL	≤1.8 ng/L	LOD (Annex B&C)	
Freedom from Contamination	5 Blanks	≤5.0 ng/L	1 Blank (5.4.5)	
Standard Check	QCS	2nd source mandated	(5.4.2)	2nd source, if possible
Signal Stability	OPR (9.4)	1/20 samples 10 ng/L ±2 s.d.	Bias	1/20 samples 90-110%[7]
Matrix Spike	MS	63-111%	(5.6.3.1)	
Matrix Duplicate	MSD	18%	(5.6.3.1)	

Table 4: Comparison of Quality Control Checks

[7] Based on permitted bias Annex A for treated sewage and trade effluents

Results

Test	Result	Comment
MDL	0.65 ng/L	
Freedom from Contamination (Blanks)	-0.35 ng/L	σ = 0.33 ng/L
Signal Stability 10 ng/L	9.98 ng/L	σ = 0.34 ng/L
Matrix Spikes	102.9%	Spike = 25 ng/L
Matrix Duplicates (%RSD)	5.6%	
Reference Standard ERA 931	43.2, 40.8 ng/L	Certificate = 42 ng/L

Table 5: System Performance and Quality Control Checks

Discussion

Both ISO/IEC17025 and the mCERTS Performance Standard are designed for a wide variety of analytes and as such have very few, if any, mandated performance criteria. With USEPA method 245.7 the quality controls are specific for mercury by the technique of cold vapor atomic fluorescence allowing mandated acceptance criteria.

References

1. BS EN ISO 17852:2008 BS 6068-2.98:2006 Water quality - Determination of mercury - Method using a combined preservation and digestion step followed by atomic fluorescence spectrometry.
2. ISO/IEC 17025 General requirements for the competence of testing and calibration laboratories.
3. EPA-821-R-05-001Method 245.7 Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry, Revision 2.0