

Atomic Absorption



The Determination of Mercury at Ultratrace Levels Using FIMS and Amalgamation Technique

Summary

The PerkinElmer® Flow Injection Mercury System (FIMS) is used in combination with an amalgamation preconcentration technique to determine Hg at ultratrace concentrations. Using a 10-mL sample volume, the instrumental detection limit is 0.3 ng/L. The method detection limit obtained in drinking water is 1.0 ng/L with a spike recovery of 100 ±4%. The operating conditions for the amalgamation system are optimized for the specific requirements of the FIMS system.

Introduction

The Flow Injection Mercury System (FIMS) is a dedicated mercury system that integrates flow injection cold vapor mercury generation with a high-sensitivity mercury detector. The use of an intense line source, a long path measurement cell and an optimized detector provides instrumental detection limits as low as 5 ng/L using a sample volume of 500 µL.

If even lower detection limits are required – for example, for the determination of mercury at ultratrace levels in surface water and drinking water samples – then the FIMS can be coupled to the amalgamation accessory, a fully automated system for the preconcentration of mercury.

In this work, the FIMS parameters and the manifold were optimized for use with an amalgamation system. This work is based on approved analytical procedures¹ and on work previously reported using other PerkinElmer flow injection systems and the amalgamation technique.²⁻³

Experimental

A PerkinElmer® FIMS-100 or FIMS-400 mercury system with an AS-90 or AS-91 autosampler and a PerkinElmer amalgamation system were used.

Figure 1 shows the FIMS/Amalgamation manifold. The manifold configuration used is based on that described in reference 2 for continuous-flow mode. Figure 2 shows details of the connections at the FI valve and the connected wash flask.

Two argon streams were used:

Purge argon flow from FIMS: approx. 60 mL/min.

Carrier argon flow from amalgamation system: approx. 80 mL/min.

When the valve is in the **Fill** position, the gas/liquid separator is connected to the **exhaust** (or waste). When the valve is in the **Inject** position, the gas/liquid separator is connected through the wash flask to the Au/Pt gauze and the cell. In this case, two argon streams, from both the FIMS and the amalgam system, flow through the Au/Pt gauze and the absorption cell. The pump tubing used is listed in Table 1. All the connecting tubes are PTFE with a 1-mm i.d.

The PTFE filter membrane normally installed in the block-type gas-liquid separator was removed when the amalgamation system was used.

FIMS operating parameters used are presented in Tables 2 and 3.

Table 1. Pump Tubing.

Solution	Color code	i.d. (mm)	Flow rate (mL/min)
Sample	blue-yellow	1.52	9 to 11
Reductant	red-red	1.14	5 to 6
Waste	black-white	3.18	28 to 32

Table 2. Spectrometer Operating Parameters.

Wavelength	253.7 nm
Signal Measurement	Peak Height
Smoothering	9 points
Read Time	20 sec.
Read Delay	0 sec.
BOC Time	2 sec.

Table 3. FIAS Operating Parameters.

Step	Time	Pump 1	Valve	Read	Heat	Cool
Prefill	15	120	Fill			
1	10	120	Fill			*
2	60	120	Inject			*
3	20	0	Inject			*
4	35	0	Fill			*
5	25	0	Fill	*	*	
6	10	0	Fill			*

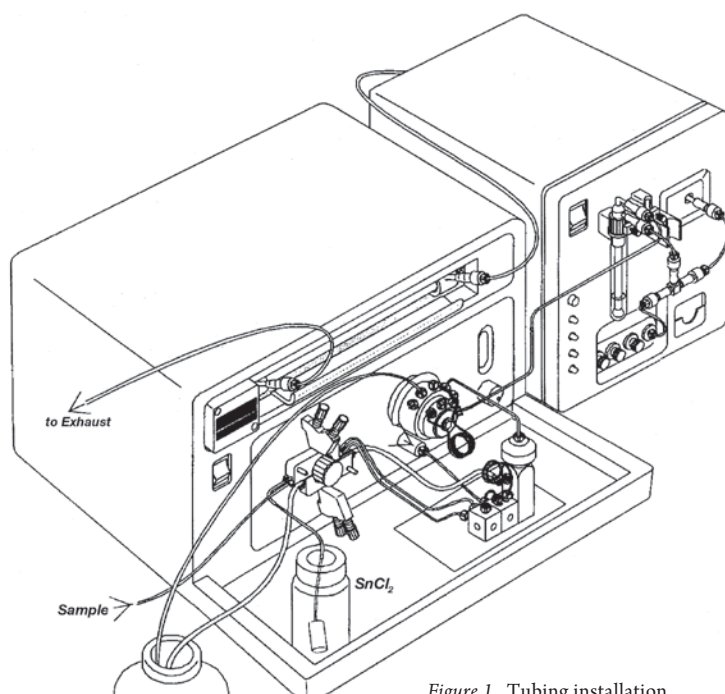


Figure 1. Tubing installation.

Reagents

The reagents used for the sample and standard preparation are listed in reference 1. The reagents used for sample analysis are listed below.

NaBH ₄ :	Riedel de Haën
HCl:	30% Suprapur, Merck
H ₂ SO ₄ :	Suprapur, Merck, Min. 96%
NaOH:	Reagent grade, Merck
SnCl ₂ •2H ₂ O:	Reagent grade, Merck

Wash solution in the wash flask

The wash flask contains 2 mL of the appropriate wash solution. A 20% (m/v) NaOH solution is used in the wash flask when NaBH₄ is used as the reductant. Since gaseous hydrides generated in the manifold can contaminate the gold/platinum gauze, NaOH is used to absorb these hydrides.

When SnCl₂ is used as the reductant, the wash flask solution is 2.5 g SnCl₂ dissolved in 7.5 mL H₂SO₄ and a small amount of water, then diluted to 50 mL with deionized or distilled water. The purpose of this wash solution is two-fold. The SnCl₂ prevents collection of any mercury in the vessel, while the H₂SO₄ acts to dry the vapor.

Procedure

All pump tubing is operated from the same peristaltic pump. The prefill step is active only during the first repetition of a

sample or standard. During this step, the previous sample solution inside the autosampler tubing is replaced by the new sample solution. Step 1 stabilizes the flow prior to pre-concentration to provide reproducible conditions for each replicate. In the prefill and in step 1, the generated mercury is transported to the waste. Steps 2 and 3 are the pre-concentration steps where Hg vapor is transported to the Au/Pt gauze. The time and the pump speed selected in step 2 define the sample volume pumped through the system for pre-concentration. Step 3 is required for complete stripping and transport of the Hg vapor generated in step 2. During steps 2 and 3 both gas flows (the stripping gas from the FIMS and the carrier gas from the amalgamation system) are active. During the heating cycle (step 5), the gas flow has to be restricted to 80 mL/min in order to obtain the highest sensitivity. This is obtained by switching the FI valve back to the "Fill" position. In this position the amalgamation portion of the system is disconnected from the mercury generator.

Due to the extremely high sensitivity of the FIMS, 35-45 seconds are necessary to stabilize the gas flow through the measurement cell to avoid baseline shifts and obtain the best possible detection limits. The gas tubing plays an important role in determining the time required to obtain stabilization of the gas flow. The tubing had to be optimized with respect to diameter and length.

In step 5 the preconcentrated Hg is released from the gauze and determined in the FIMS photometer. Step 6 provides a cool-down time for the gauze prior to the pre-concentration of the next sample.

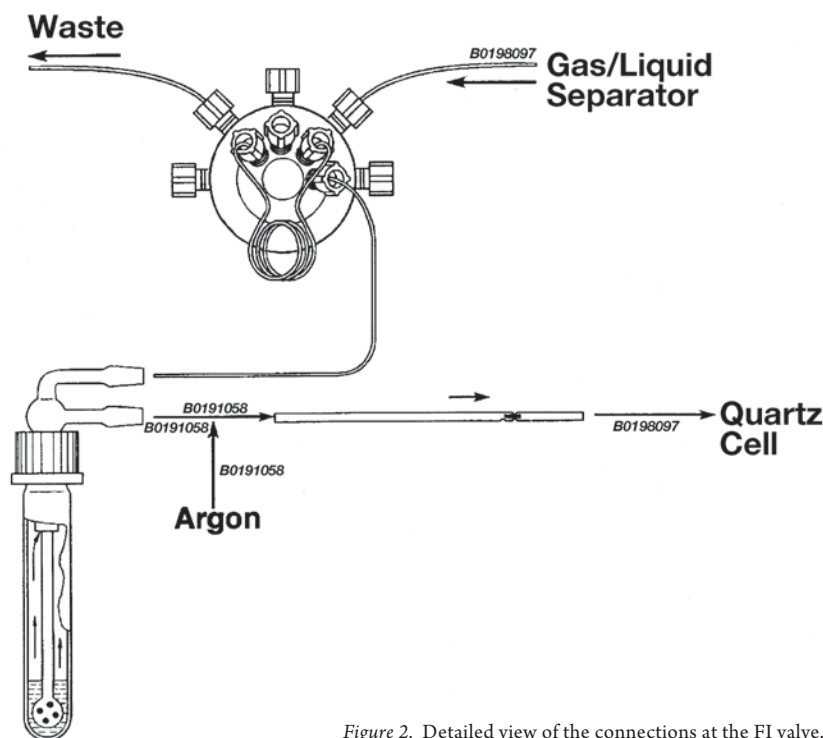


Figure 2. Detailed view of the connections at the FI valve.

Results

The mercury content in surface water samples from Lake Constance and samples from Lake Constance Water Supply, Überlingen, Germany, were analyzed. Both samples contained 1 ng/L Hg. This is in agreement with results provided by Lake Constance Water Supply using the method described in reference 1: sample digestion with an ultrasonic bath and cold vapor Hg measurement following amalgamation using SnCl_2 as the reductant.

Tap water samples from the city of Überlingen and Lake Constance surface water were spiked with 10 ng/L Hg.

The results of the recovery tests are as follows:

Drinking water: $102 \pm 2\%$

Lake water: $98 \pm 2\%$

At 10 ng/L Hg, the RSD was approximately 3-4% for three replicates. The useful application range of this method is 1.0 ng/L to 200 ng/L with a 7-mL sample volume. Absorbance peaks for a blank, 10, 20 and 50 ng/L are shown in Figure 3. The preconcentration time used was 60 seconds and the sample volume approximately 7 mL. Increasing the preconcentration time to 90 seconds further enhances the Hg readings (Figure 4), allowing even lower concentrations to be detected.

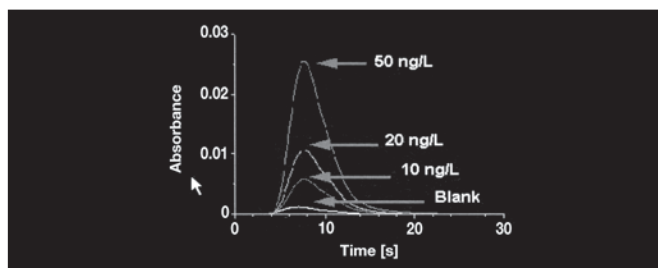


Figure 3. Signal shape of aqueous standard solutions, 60 seconds amalgamation.

Discussion

The excellent precision and detection limits of the FIMS system are the result of an exceptional signal-to-noise ratio and the highly stable baseline, even at 0.0001 absorbance levels. As variations in the carrier gas flow may disturb the baseline stability, the tubing installation and the FIAS program are optimized for optimum gas flow stability. Detection limits below 1 ng/L can be reached easily.

Detection limits can be further reduced by using larger sample volumes (i.e., longer amalgamation times). However, reagent contamination normally becomes the limiting factor in establishing detection limits. Therefore the use of high purity, "mercury-free" reagents and ultra-clean laboratory vessels is strongly recommended.

References

1. German standard methods for the examination of water, waste water and sludge; Cations (group E); determination of mercury (E 12). DIN 38406/12.
2. S. McIntosh, The Determination of Mercury at Ultra-Trace Levels Using an Automated Amalgamation Technique, Technical Summary, PerkinElmer, Inc.
3. Amalgam System, Accessory for use with the FIAS-200 Flow Injection System, Operator's Manual.

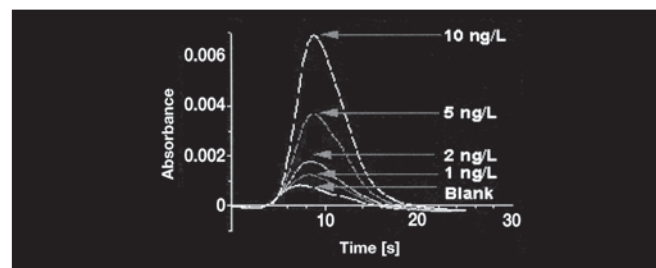


Figure 4. Signal shape of aqueous standard solutions, 90 seconds amalgamation.