# Using FIMS to Determine Mercury Content in Sewage Sludge, Sediment and Soil Samples

## Introduction

The Flow Injection Mercury System (FIMS) is a dedicated system that integrates flow injection mercury cold vapor generation with a very sensitive detector. The exceptional system stability and the long path measurement cell provide instrumental detection limits as low as 5 ng/L using a sample volume of 500 µL.

The improved sensitivity of the FIMS permits sample dilution, therefore reducing the likelihood of an interference occurring with complex samples.

In this work, samples were digested with aqua regia using reflux conditions according to DIN method 38414. After proper dilution of the digested sample solution, Hg was measured interference-free using $SnCl_2$ as the reductant.

The recoveries of spiked mercury in sewage sludge samples ranged from 96 to 100%. The method was checked by the analysis of standard reference materials. All results were in agreement with certified values. The RSD for three replicates was approximately 2% at 10 µg/L Hg level.

The sample solutions were also measured using a FIAS to generate the Hg vapor and the analytical data were collected using an AA spectrometer equipped with a $D_2$ background corrector. The results are in agreement with those obtained using the FIMS, which demonstrates that any background absorption for these determinations was negligible.

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## Instrument setup

PerkinElmer® FIMS 400 mercury analyzer with AS-91 Autosampler.

Default FIAS conditions are shown in Table 1. The pump tubing is listed in Table 2. The operating parameters are summarized in Table 3.

Sample volume:          500 µL

Carrier gas flow rate: 70-80 mL/min

**Table 1. FIAS Program.**

| Step | Time (s) | Pump 1 (rpm) | Pump 2 (rpm) | Valve | Read |
|------|------|------|------|------|------|
| Prefill | 15 | 100 | 120 | Fill | |
| 1 | 10 | 100 | 120 | Fill | |
| 2 | 20 | 0 | 120 | Inject | * |

**Table 2. Pump Tubing Used.**

| Pump Tube | I.D. (mm) | Color Code | Flow Rate (mL/min) |
|------|------|------|------|
| Pump 1 Sample | 1.52 | Yellow/Blue | 9-11 |
| Pump 2 Carrier | 1.52 | Yellow/Blue | 9-11 |
| Reductant | 1.14 | Red/Red | 5-6 |
| Waste | 3.18 | Black/White | 32-35 |

**Table 3. Operating Parameters.**

| | |
|------|------|
| Wavelength | 253.7 nm |
| Signal Measurement | Peak Height |
| Read Time | 20.0 sec. |
| Read Delay | 0.0 sec. |
| BOC Time | 2 sec. |

## Reagents and solutions

All chemicals were at least of analytical reagent grade, and deionized water was used throughout.

| | |
|------|------|
| $SnCl_2 \bullet 2H_2O$: | Pro analysi Merck |
| $HNO_3$: | Pro analysi Merck (max. 0.0000005% Hg) |
| HCl: | Pro analysi Merck, 37% (max. 0.0000005% Hg) |
| $K_2Cr_2O_7$: | Pro analysi Merck |
| Antifoaming Reagent: | Dow Corning 110 A |

**$SnCl_2$ solution:** 1.5% m/v in 1% v/v HCl. Dissolve 15 g $SnCl_2 \bullet 2H_2O$ in about 150 mL water containing 10 mL HCl, then dilute the solution to 1 L. To 1 liter of this solution, add 200 µL antifoaming reagent.

**Carrier solution:** 3% v/v HCl. Dilute 30 mL HCl to one liter with deionized water.

**Stabilizing solution:** 0.5% m/v $K_2Cr_2O_7$ in 1+1 $HNO_3$ Dissolve 0.5 g $K_2Cr_2O_7$ in 50 mL water, then add 50 mL concentrated $HNO_3$.

**Calibration Standards:**

Stock standard mercury solution #1, 1000 mg/L, was prepared from Merck "Titrisol®".

Stock mercury solutions #2 and #3: 10 mg/L and 1 mg/L, respectively, were prepared by further dilution of the stock standard solution #1.

Calibration standards at different mercury levels were prepared from stock solutions #2 and #3 by further dilution in 3% v/v HCl.

Calibration standard solutions used for the measurement of sewage samples were 0.00, 5.00, 10.00, 15.00, 20.00, and 30.00 µg/L.

Calibration standard solutions used for the measurement of soil and sediment samples were 0.00, 3.00, 5.00, 7.00, and 10.00 µg/L.

According to DIN 38 405-E 121, the standard solutions should contain 1% v/v of the stabilizing solution.

## Procedure

### Sample Digestion and Pretreatment

Weigh 3.00 ±0.01 g into the digestion flask, moisten the samples with a few drops of water, add 21 mL HCl and 7 mL $HNO_3$. Pipette 10 mL $HNO_3$ into the absorbing vessel (refer to the digestion apparatus description in DIN 38414, Part 12). Then start the digestion procedure under reflux conditions, also according to DIN 38414, Part 12. If the samples foam after the addition of acids, let the mixture stand overnight before starting the digestion.

After cooling, transfer the solutions from the digest flask into a 100 mL volumetric flask, dilute to volume with deionized water and mix well. After allowing the undigested material to settle out or after filtration, take 1 mL of the clear supernatant solution into 10-mL test tube, add 100 µL of $K_2Cr_2O_7$ stabilizing solution, dilute the mixture to 10 mL and mix well. This solution is then ready for measurement.

For very reactive samples, use the glass type gas-liquid separator.

## Recovery study

A recovery study was conducted for sewage samples as follows:

Add 1 mL of the clear supernatant solution to a 10-mL test tube, add 100 µL of $K_2Cr_2O_7$ stabilizing solution, spike with 1 mL of 0.10 mg/L Hg standard solution, then dilute the mixture to 10 mL and mix well. The spiked Hg concentration in the diluted solutions was 10 µg/L.

## Measure standard reference materials

To check the accuracy and reliability of this method, the following standard reference materials were used in this work:

NBS 1645:   River Sediment

BCR 142:   Light Sandy Soil,
No. 487 (individual identification)
No. 528 (individual identification)

BCR 145:   Trace Elements in a Sewage Sludge,
No. 310 (individual identification)

BCR 146:   Trace Elements in a Sewage Sludge
of Mainly Industrial Origin,
No. 265 (individual identification)

BCR 142, 145 and 146 are certified reference materials from the Community Bureau of Reference, Commission of the European communities.[2]

### Measurement with $D_2$ Background Corrector

Prepared solutions of the above materials were also analyzed with a FIAS-400 and a PerkinElmer Model 4100 equipped with a $D_2$ background corrector to check for background absorption. A Mercury System II EDL was used as the light source.

To learn more about the concentration levels of other coexistent metal ions in the samples, the solutions were also analyzed semi-quantitatively for Cu, Ni, Pb and Zn using a PerkinElmer Optima™ 3000 ICP-OES spectrometer.

## Results

Four sewage sludge samples and a previously-digested soil sample were analyzed using the FIMS. The analytical results are listed in Table 4 compared with the results obtained using the Model 4100 and $D_2$ background correction. Recoveries of spiked Hg (II) in sewage sludge sample solutions ranged from 96-100%.

The values listed in the table are the mean ± standard deviation for n separate measurements.

The semi-quantitative results (µg/g) for coexisting elements in sewage sludge samples 1-4 using the Optima 3000 ICP-OES spectrometer are as follows:

Cu:  330-550

Ni:  35-120

Pb:  72-150

Zn:  1100-2800

The concentrations of these constituents are similar to those found in BCR 145.

The measured results and the recommended values of standard reference materials are summarized in Table 5.

*Table 4.* **Measured Results of Sewage Sludge and Soil Samples.**

| | FIMS µg/g | Model 4100 with $D_2$ µg/g | Recovery % |
|---|---|---|---|
| Sew. Sludge 1 | 1.20 ±0.05 n = 3 | 1.17 ±0.04 n = 2 | 98 |
| Sew. Sludge 2 | 3.33 ±0.05 n = 3 | 3.34 ±0.04 | 96 |
| Sew. Sludge 3 | 3.00 ±0.07 n = 3 | 2.96 ±0.04 n = 2 | 96 |
| Sew. Sludge 4 | 2.09 ±0.03 n = 3 | 2.09 ±0.05 n = 2 | 99 |
| B 3671 (Soil)* | 297.9 ±2.9* n = 3 | 316.9 ±6.8* n = 2 | |

*\* This sample is a digested solution supplied by an external laboratory. The units for these results are µg/L.*

*Table 5.* **Measured Results of Reference Materials.**

| Sample No. | Measured Value µg/g | Recomm. Value µg/g |
|---|---|---|
| NBS 1645 | 1.1 ±0.1 n = 4 | 1.1 ±0.5 |
| BCR 142 No. 487 | 0.112 ±0.007 n = 5 | 0.104 ±0.012 |
| BCR 142 No. 528 | 0.113 ±0.009 n = 5 | 0.104 ±0.012 |
| BCR 145 No. 310 | 9.48 ±0.19 n = 3 | 8.82 ±0.88 |
| BCR 146 No. 265 | 9.09 ±0.11 n = 3 | 9.49 ±0.76 |

The listed values in the table are the mean ± standard deviation for n separate measurements.

Figures 1 and 2 are the recorded signal traces for Sewage Sludge sample No. 2 and BCR 145.

## Discussion

Stabilizing solution was added to the diluted sample solutions to keep mercury content stable. It was found that the mercury content in diluted sample solutions continuously decreased without the addition of the stabilizing solution.

When using $SnCl_2$ as a reductant, interferences have been reported for waters containing sulfide, chloride, copper and tellurium. Also, organic compounds which have broad band UV absorbance (around 253.7 nm) are confirmed interferences.[1,3] Iodide has also been reported to interfere with the measurement.[1,4] In general, there are less severe interferences from heavy metal ions when $SnCl_2$ is used as a reductant compared to the use of $NaBH_4$ as the reductant. Proper dilution of the sample solutions can alleviate interferences.[1]

It was found in this work that the digested sample solution must be diluted (e.g., 1 to 10) prior to measurement. Otherwise, even when 10% w/v $SnCl_2$ was used as the reductant, the measured results were low. Since the FIMS system is highly sensitive and provides improved mercury detection limits, it is possible to measure the low Hg levels even with dilution of the sample solutions.

It has been reported that there is a risk of interference from volatile nitrogen oxides when mercury is determined by FI-CVAAS in digests of samples which have been decomposed by nitric acid.[5] In this work, concentrated *aqua regia* was used for the sample digestion. Nitrogen oxides were generated during the digestion process, especially for the sewage sludge sample, because these samples contain large amounts of organic material. However, no interference or background signals were observed. The background signals of the diluted sample solutions measured with a $D_2$ background corrector were negligible, as shown in Figure 3.

## Conclusion

After digestion using the DIN method, the mercury levels in sediment, sewage sludge and soil samples were determined using FIMS with $SnCl_2$ as reductant. The measurement is precise, simple and fast.

Relatively high Cu, Ni, Pb and Zn contents were found in the sewage sludge samples. However, by using $SnCl_2$ as the reductant and diluting the sample solutions, the measurements were virtually interference-free. Similarly, no interferences from volatile nitrogen oxides or other nonspecific absorption signals were observed.
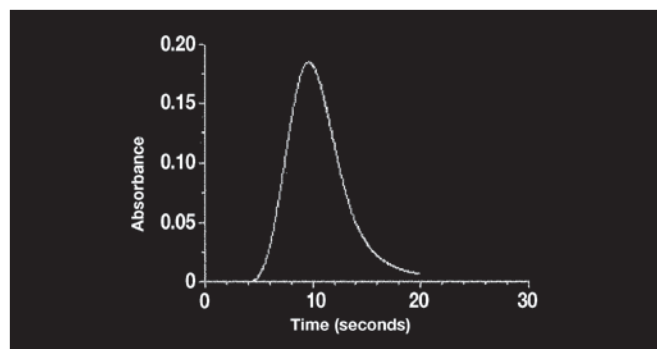


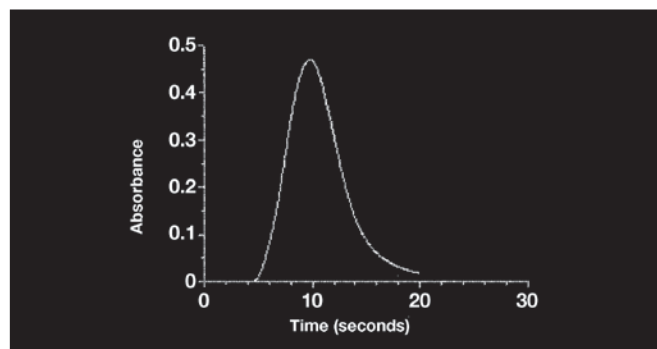*Figure 1.* Absorbance signal of sewage sludge sample 2.
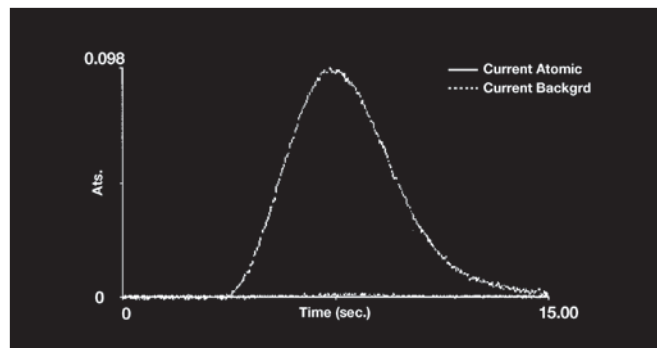


*Figure 2.* Absorbance signal of BCR 145 (sewage sludge).



*Figure 3.* Signal traces of sludge sample 2 measured using a Model 4100 with $D_2$ background corrector.

## Reference

1. Deutsche Einheitsverfahren zur Wasser, Abwasser und Schlammuntersuchung Kationen DIN 38 405-E 12.

2. Community Bureau of Reference-BCR, Certified Reference Material, Certificate of Analysis, Brussels, June 1983.

3. EPA Method 245.1 Revision 2.3 April 1991, U.S. Environmental Protection Agency.

4. B. Welz and M. Schubert-Jacobs, Fresenius Z Anal Chem (1988) 331:324-329.

5. Inge Rokkjaer, Boy Hoyer, and Nina Jensen, "Interference by Volatile Nitrogen Oxides in the Determination of Mercury by Flow Injection Cold Vapor Atomic Absorption Spectrometry".

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