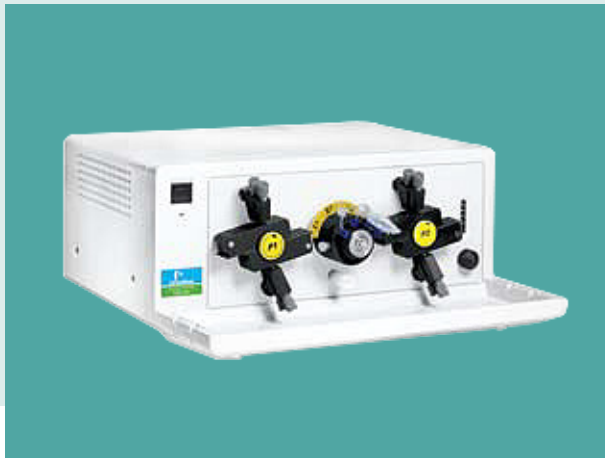
TECHNICAL NOTE

Recommended Analytical Conditions and General Information for Flow Injection Mercury/Hydride Analyses Using the PerkinElmer FIAS 100/400

Atomic Absorption



General Information

In order to become familiar with the features and operation of the Flow Injection Mercury/Hydride System (FI-MHS), it is strongly recommended that the analyst work through the example described in the FI-MHS manual when operating the system for the first time.

Calibration and Analysis

With the FI-MHS system, calibration and sample analysis are similar to the corresponding procedures for automated flame atomic absorption (AA).

Sensitivity

Relative or solution sensitivity (µg/L of analyte to produce a signal of 0.0044 A) for FI-MHS is comparable with that obtained using other MHS techniques. Because FI-MHS requires much smaller sample sizes, however, the absolute sensitivity (nanograms of analyte to produce a signal of 0.0044 A) attainable is significantly lower than for most other MHS techniques.

The sensitivity of FI-MHS determinations can, within limits, be adjusted to suit the concentration of the samples by varying the volume of the injection loop or by changing the analytical wavelength.

Sample Volumes

Sensitivities listed in the "Recommended Analytical Conditions" section are based on sample volumes of 500 µL. Larger sample volumes typically do not produce significantly better sensitivity and require longer measurement times. For maximum throughput, sample volume should be kept as low as possible.

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Replicates

As FI-MHS normally requires only 0.5 mL (500 µL) or less for each determination, the solution in one autosampler vial can be used for a number of replicates. However, since reproducibility for FI-MHS is very good, the number of replicate determinations necessary to obtain required precision levels is usually small.

Potential Interferences

As the analyte is separated from the sample matrix, MHS techniques are largely free of the chemical, matrix, and background absorption interferences found with flame AA. Those interferences, which may potentially occur with FI-MHS, are generally associated with sample or standard preparation or gas or liquid flow through the system.

For example, some samples tend to produce either excessive foam or precipitates when $NaBH_4$ is added. Both phenomena can affect analytical results and should be avoided, if possible. It is advisable to test unknown sample types to determine if they exhibit foaming characteristics or if precipitates are generated upon addition of the reaction reagents. The preliminary testing can be carried out in a laboratory hood using a tall, open beaker.

Foaming

If excessive foaming results in liquid being transported into the quartz cell, the reagent stream should be stopped immediately, and the tubing and cell assemblies should be disassembled and cleaned.

Excessive foaming can usually be avoided by placing 1% of an antifoaming agent into the reductant solution. The following antifoaming agents have been successful:

- Antifoam Emulsion: 110A Dow Corning
- Silicon Antifoaming Agent: Type 107743, Merck KGaA
- Antifoam Emulsion 110A can be purchased from PerkinElmer as Part Number B0507226.

Precipitates

All solutions used with the FI-MHS (samples, carrier solutions, and reducing agents) must be free of solid particles since they are transported through narrow tubing and valve openings. In addition, the formation of precipitates during the course of a reaction must be avoided. For example, precipitates may be formed when protein-containing samples come in contact with acids or when samples with high metal content come in contact with sodium borohydride. In such cases, an appropriate digestion or separation method should be used to remove the offending component.

Contamination

The detection limits obtainable using the FIAS system are very often a function of the degree of contamination in the samples and reagents rather than of instrumental capabilities. Contamination is the main source of error when working at the nanogram levels typical for FI-MHS analyses. Careful operation of the instrument, selection of proper sample preparation techniques and good laboratory cleanliness practices are the most important prerequisites for minimizing contamination.

Risk of contamination can also be reduced by:

- Using only high purity double-distilled or, preferably, deionized water for the preparation of reducing solutions, standard solutions and sample solutions and for dilutions.
- Ensuring that all materials which come into contact with the water or solutions are made of clean inert plastic. Pure water or solutions can quickly become contaminated by impurities from the container in which they are stored, even if the container is made of PTFE.
- Preparing the reagent solutions from chemicals of the highest purity.

> Note: The blank concentration of the analyte element in the reducing agents and all othe chemicals required for the analysis must be determined before use.

Background Correction

The use of a background corrector is, in general, not required with the FI-MHS since the analyte element is almost completely separated from the matrix before atomization. Nevertheless, it is advisable to conduct a test using background correction on samples whose composition is unknown in order to check that the results are indeed element specific and that nonspecific absorption has not led to inaccuracy.

At wavelengths below 200 nm, which includes the resonance lines for As and Se, there is significant absorption of source radiation by the hot air in the atomizer cell. Although not required, the use of background correction will automatically compensate for this absorption.

Standard Solution

Standard solutions for use with the FIAS 100/400 can be prepared by appropriate dilution of stock solutions. All standard solutions should be stored in inert plastic containers. Stock solutions with a concentration of 100 mg/L or more can usually be kept for one year. Solutions with a concentration of 1 mg/L or less should be prepared daily. For all solutions with concentrations less than 10 mg/L, the water used for dilution and any acids or other added reagent must be checked for contamination by the analyte element.

The stability of Hg standards can be strongly affected by adsorption onto the walls of the storage vessel. It is recommended that Hg standard solutions be prepared in a mixture of 2% (v/v) HNO_3 and 2% (v/v) H_2SO_4, with the addition of 1-2 drops (approx. 30-60 µL) of a 5% (w/v) $KMnO_4$ solution to stabilize the standard.

System Maintenance

The FIAS systems require little maintenance. After use, the system should be carefully rinsed with deionized water and then the water should be pumped out. The peristaltic pump rollers should then be released so that the tubing is not compressed.

Peristaltic Pump

The peristaltic pump roller pressure and the elasticity of the tubing can have an effect on pump performance and sensitivity. Both should be checked daily and adjusted or replaced as necessary.

Quartz Cell Conditioning

Sensitivity, especially for As, Sn and Te, is heavily dependent on the condition of the quartz cell. If the sensitivity check given in the Recommended Standard Conditions cannot be achieved, it may be necessary to condition the quartz cell in concentrated hydrofluoric acid as described below.

Note: The quartz cell is conditioned in the factory before shipment. Before conditioning the cell as described below, make certain that there are no other causes for the loss in sensitivity, such as standards or reducing solutions which have been left standing too long, or improper spectrometer or FIAS system parameter settings.

Important: Extreme caution is required when working with hydrofluoric acid. The work must be performed in a properly ventilated fume hood and protective clothing (rubber gloves, rubber apron, and face shield) should be worn at all times.

- Remove the windows from the quartz cell as described in the instructions.
- Place the cell in a bath of cold concentrated hydrofluoric acid (40%) for 20 minutes.
- Thoroughly rinse the cell under running water, then rinse it in deionized water and dry it.
- Reassemble and install the cell.

Pump Tubing

The integrity of system tubing and tubing connections should be checked periodically and replaced as required. The dimensions of the pump tubing assemblies are critical for trouble-free operation and to obtain the quoted sensitivities. If tubing assemblies are to be replaced, they should be replaced with exact duplicates with the same length, I.D., O.D., tubing composition, and connectors. Of particular importance are the tubing assemblies for the transport of the carrier stream and the reducing agent.

Other tubing assemblies are less critical. The only criterion for the tubing used to remove waste is that it must be sufficiently large to prevent flooding of the gas/liquid separator. The diameter of the pump tubing for the sample need only be large enough to ensure that the sample loop is totally filled with sample solution in the prescribed time.

Other Tubing Considerations

In general, all FIAS system tubing connections should be as short and as small in diameter as possible. Long tubing with a large diameter creates broader, flatter signals which produce reduced sensitivities and poorer analytical performance.

Reaction Loops

In some cases, it may be advantageous to insert an additional reaction loop through which the reaction mixture flows before reaching the gas/liquid separator. In this way, a reduction requiring a longer reaction time can take place within the system. Under certain circumstances, the digestion procedure can therefore be shortened or prereduction avoided. For example, arsenic (V) is incompletely reduced and converted to the hydride with standard conditions. With the addition of a reaction loop, the longer contact or reaction time may permit arsenic (V) to be measured directly without prereduction.

However, a reducing loop should not be used regularly or indiscriminately. Due to the increased reaction time, interferences may arise. Also, any lengthening of the tubing also increases the required analysis time and results in a lower and broader signal, decreasing sensitivity with peak-height measurement.

Factors Affecting Hydride Generation Using Flow Injection

The successful analysis of samples using flow injection-hydride generation requires the operator to be familiar with proper setup and operation of a flow injection system.

Initial Checks

When setting up the FI-MHS, the operator must install peristaltic pump tubing, a gas/liquid separator and a reaction unit. After ensuring that all connections are secure, the flow rates in each of the supply tubes should be measured. Consult the operator's manual for proper procedures on measuring flow rates. Consistent flow rates ensure that the performance of the system is reproducible over the long term. Also, monitoring flow rates can indicate when pump tubing should be changed or connectors cleaned.

Once the flows of the reductant, carrier and sample are determined, a standard of the proper concentration (noted in the Recommended Conditions) should be run to check the sensitivity. If the sensitivity is in good agreement with the recommended sensitivity check value, the user can proceed with samples. If the sensitivity is low, the user should refer to the following section.

Factors Affecting Sensitivity

Low sensitivity can be attributed to either hardware or chemical factors. Deciding where the problem exists requires a basic understanding of the hydride technique.

The hydride technique involves the reaction of acidified aqueous samples with a reducing agent, such as sodium borohydride. The sodium borohydride/acid reduction generates hydrides as shown in the following equations.[1]

$$NaBH_4 + 3H_2O + HCl \rightarrow H_3BO_3 + NaCl + 8H \quad \text{[Eq. 1]}$$

$$E^{m+} + H(\text{excess}) \rightarrow EH_n + H_2(\text{excess}) \quad \text{[Eq. 2]}$$

where E = analyte of interest and m may or may not equal n

This reaction generates a volatile hydride which is transported to a quartz cell by means of an argon carrier gas. In the quartz cell, the hydrides are converted to gaseous metal atoms.

It is believed that atomization of the hydride occurs from collisions with free hydrogen radicals.[2,3] In the quartz cell, the generated analyte atoms are contained in the path of a source lamp and a signal is generated by measuring the amount of light absorbed. Low sensitivity results if there is a problem in generating the hydride, transporting the hydride to the quartz cell or atomization of the hydride.

The factors which can affect the generation of the hydride can be as simple as not using freshly prepared reductant. This can be avoided by preparing the reductant daily and preserving it with sodium hydroxide. The purity of all reagents used is critical when determining low levels of hydride-forming elements.

Care should be taken to ensure that all reductants, acids and reagents are free from the elements being determined and any elements which may react with the generated hydride.

Another factor affecting the sensitivity is the oxidation state of the analyte. In solution, arsenic, selenium, antimony, bismuth and tellurium can exist in two different oxidation states. The oxidation state affects the rate at which the metal-hydride is formed and thus the sensitivity. To ensure that all of the analyte exists in the same oxidation state, all standards and samples should be carried through a reduction procedure. Refer to the following recommended conditions to find the correct reduction procedure for each element.

With flow injection, the sensitivity of the analysis depends on the amount of sample used for the determination. The volume of sample used for the analysis is determined by the size of the sample loop located on the injection valve. A typical analysis uses 500 µL of sample. However, the sensitivity can be altered by decreasing or increasing the size of the sample loop.

The amount of time permitted for the reaction of the sodium borohydride and sample may also affect the sensitivity. The reaction time is determined by the length of the reaction coil, which is the coil joining the reductant and sample inlets to the argon inlet in the chemifold. The use of a longer reaction coil results in increased reaction times. For most elements, the recommended 300 mm reaction coil is sufficient, but if a different reaction time is desired, the length of this coil may be changed.

The generated hydride is collected in the gas/liquid separator and then transported to the quartz cell. The volume collected is dependent on the waste removal from the separator. If the removal of waste occurs too quickly, the hydride gas can be carried to the waste container and the resulting sensitivity will be low.

The removal of liquid from the gas/liquid separator can be controlled by adjusting the tension on the waste pump tubing such that the liquid fills approximately one third of the separator. Care should be taken to avoid allowing the separator to become overfilled, as this may result in moisture collecting on the membrane or in the transfer line. This moisture may interfere with the transport of the hydride to the quartz cell.

The actual transfer of the collected hydride is controlled by the use of an argon carrier gas. When argon flow rates are too high, the metal-hydride can be carried out of the quartz cell too quickly. This reduces the residence times of generated atoms, resulting in low sensitivity. If the flow rate of the carrier gas is too low, the more unstable hydrides, such as tin, may actually decompose during the transfer of the hydride resulting in low sensitivity. Optimization of the carrier gas flow will ensure maximum sensitivity for each analyte.

The atomization of the hydride occurs in the quartz cell. It has been shown that the surface of the quartz cell can have a dramatic effect on the sensitivity and precision of arsenic, antimony, selenium and tin determinations.[4-7]

If it is suspected that the quartz cell is contributing to low sensitivity, the cell should be cleaned in a bath of concentrated hydrofluoric acid for twenty minutes and then rinsed with deionized water. Allow the quartz cell to completely dry before reusing.

> Note: Caution is required when using hydrofluoric acid. Use proper laboratory safety procedures.

Factors Affecting Precision

The precision of a flow-injection hydride analysis is dependent on the reproducible injection of a sample volume into a continuously flowing carrier stream. This is achieved by ensuring that all connections are secure, with no evident leaks, and by proper programming of the flow injection system. Suspended solids would be removed from all solutions to ensure consistent unimpeded flow of the sample and reagents.

The flow injection software controls the sequence of the determination using three basic steps. The first, a prefill step, is for filling the tubing from the autosampler to the valve, and is used only for the first replicate to minimize analysis time and sample consumption. The second step is for filling the sample loop, and the third step injects the sample into the carrier stream. These last two steps are used for all replicates.

If the precision of the analysis is poor, the analyst should check to see if there is a pattern. For example, if the first replicate of a series is low, this would indicate that the time allotted for filling the autosampler tubing is insufficient and should be increased. If the first replicate of the series is high and the subsequent readings are low, this may be an indication that the time for filling the sample loop should be increased.

Efficient transport of the hydride from the gas/liquid separator to the quartz cell can also effect the precision of the analysis. Care should be taken to ensure that the waste removal from the separator is consistent and that the carrier gas flow rate is properly adjusted.

Periodically, the one-way valve connected to the argon outlet should be removed and cleaned to ensure that the gas flow is not disrupted.

Recommended Analytical Conditions

The recommended analytical conditions described here allow all of the common hydride-forming elements and mercury to be determined using the same tubing and a single basic FIAS program. Optimization of specific parameters may improve analytical performance somewhat for individual elements. Such optimization may provide better sensitivity or permit the measurement of different oxidation states. If information on optimized conditions exists for an element, it is provided under the recommended analytical conditions for that element.

Spectrometer

Light Sources

The FIAS system can be used with both hollow cathode lamps (HCL) and electrodeless discharge lamps (EDL). EDLs typically provide higher energy than the corresponding HCLs and can improve sensitivity and detection limits for some elements, e.g., As and Se. EDLs typically require at least 30 minutes warm-up time for stabilization.

Wavelength and Slit

The wavelength and slit combinations producing the best sensitivity for Hg and the hydride-forming elements are found in the "Recommended Analytical Conditions" for each element. Other wavelengths may be used to reduce sensitivity for samples which produce an excessively high absorption signal but for which dilution is undesirable. For information on other available wavelengths, consult the "Cookbook", *Analytical Methods for Atomic Absorption Spectrophotometry,* supplied with all PerkinElmer® AA instruments.

Data Processing

Evaluation of FIA data may be based on either peak height or peak area. Experience has shown that peak-area evaluation provides no analytical advantages. As peak-height measurements can be performed in less time than peak-area measurements, peak-height measurement is normally the preferred quantitation procedure for FIA-mercury/hydride analysis. The integration time should be set such that the absorption signal maxima occurs within the selected time.

With peak-height measurement, the analytical precision can be optimized by proper selection of the "peak height smoothing" window available with WinLab32™ for AA software. That value is entered in the smoothing selection (e.g., 19 points) and represents the number of points used in the smoothing routine. Use of too small a value can cause reduced precision, while use of too large a value will reduce the signal magnitude. Optimum values are shown in the "Recommended Analytical Conditions" for each element.

FIAS System

The FIAS system can accommodate nine (9) complete program steps with all parameters being variable in each step. Tables 1 and 2 show typical programs for the FIAS 100 and FIAS 400.

Pump Speeds

Table 1. Programming for the FIAS 100.

Step	Time	Pump Speed	Valve Position		Read
#	(S)	Pump 1	Fill	Injection	
Prefill	15	120	*		
1	10	120	*		
2	15	120		*	*

Table 2. Programming for the FIAS 400.

Step	Time	Pump Speed		Valve Position		Read
#	(S)	Pump 1	Pump 2	Fill	Injection	
Prefill	15	100	120	*		
1	10	100	120	*		
2	15		120		*	*

Other Program Parameters

Each step also includes the time interval for each step, the position of the FIA valve (Fill or Inject), the time at which the Read function should be actuated. The recommended analytical conditions for each element also show the recommended cell temperature.

Peristaltic Pump Tubing

As noted in the General Information section, it is important to use pump tubing of the proper length and diameter. For example, the use of peristaltic pump tubing with a smaller diameter than that specified in the "Recommended Analytical Conditions" will result in a decrease in peak-height sensitivity.

The pump tube for the waste must be sufficiently large to prevent flooding in the gas/liquid separator. For the standard applications, the pump tubing shown in Table 3 is used. If more reagents are pumped, it may be necessary to use two pump tubes (violet-violet) to sufficiently drain the gas/liquid separator.

PTFE Tubings

To minimize dispersion, all PTFE tubing should be as short as possible and the inner diameter should be as narrow as possible. Longer tubing and wider inner diameter tubing will result in lower and broader signals. In the Recommended Conditions, the tubing connecting the confluence point of the carrier and reductant solutions to the argon carrier gas should be kept to a minimum length. This tubing is often referred to as the "reaction coil" and can be increased to prolong reaction times when necessary, as in the case of As^{5+}. The sensitivity may also be increased by using a longer "stripping coil". This is the tube which transports the gas/liquid mixture into the gas/liquid separator.

Table 3. Recommended Pump Tubing.

			Tubing	
			I.D.	Color
	FIAS 100	FIAS 400	(mm)	Code
Sample	P1	P2	1.52	blue-yellow
Carrier	P1	P2	1.52	blue-yellow
Reducing agent	P1	P2	1.14	red-red
Waste	P1	P2	3.18	black-white

Note: The waste pump tubing listed in the table can be applied for most applications. If more than one reagent is pumped, two waste pump tubings in parallel should be used.

Reagents

Carrier Solutions

For all elements except tin and mercury, the carrier solution is a 10% (v/v) hydrochloric acid solution (i.e., 10 parts concentrated HCl diluted to 100 parts with water). For tin, the appropriate carrier solution is a mixture of saturated boric acid (approximately 50 g/L) in 1% (v/v) hydrochloric acid. For mercury, the recommended carrier solution is 3% (v/v) HCl acid. The carrier solution must always contain the same acid, usually in the same concentration, as the sample solutions.

Reducing Agents

The normally recommended reducing agent is an aqueous solution of 0.2% (w/v) $NaBH_4$ in a 0.05% (w/v) NaOH solution, which should be freshly prepared. Filter the reducing solution before use, preferably using vacuum filtration.

If Hg is to be determined using $SnCl_2$ as the reducing agent, the reducing solution should consist of 1.1 (w/v) $SnCl_2$ (from $SnCl_2 \bullet 2H_2O$) in 3.0% (v/v) hydrochloric acid. The recommended analytical conditions using $SnCl_2$ are described in method Hg1.

Carrier Gas Flow

The carrier gas stream has a large influence on sensitivity. If the flow is too high, the atom or hydride cloud is dispersed too rapidly. If the flow is too low, the resulting signal and sensitivity are lower. A flow of 50 mL/min for the carrier stream is suitable for most elements. To obtain the highest sensitivity, optimize the flow for each element. Where a different flow may be necessary for optimum conditions, the possible range is included in the Notes section.

References

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As FI-MHS Recommended Analytical Parameters for Arsenic

Parameters

Technique	AA
Wavelength	193.7 nm
Integration Time	15 sec.
Data Processing	Smoothing: 19 points
Cell Temperature	900 °C

Reagents

Carrier Solution	10% (v/v) HCl
Reducing Agent	0.2% $NaBH_4$ in 0.05% NaOH
Sample Solution	As^{3+} in 10% (v/v) HCl

Sensitivity Check

Analysis of 500 µL of a 10 µg/L arsenic solution should provide a signal of about 0.45 A. Data obtained using an EDL. With a HCl about 0.300 A.

Notes

A higher concentration of reducing agent (e.g., 0.5%) can produce improved sensitivity.

The nature of the quartz cell surface is an important factor in obtaining proper sensitivity. If sensitivity is low, the cell may have to be conditioned.

Samples to be analyzed for As should be prereduced prior to analysis. Use a reducing solution containing 5% (w/v) KI and 5% (w/v) ascorbic acid and allow the treated samples or standards to stand at room temperature for 30-60 minutes prior to analysis.

The above mentioned sensitivities are for As^{3+}. If the arsenic exists as As^{5+}, the sensitivity will be 5-10% of the above stated values. Therefore, the samples should be reduced to As^{3+} prior to analysis. The reduction rate is faster as the acid concentration increases. To ensure proper reduction, the following procedure may be used: To 1 mL of sample or reference solution add 1 mL conc. HCl and 1 mL 5% (w/v) KI and 5% (w/v) ascorbic acid. Wait 45 minutes at ambient temperature and dilute to 10 mL. If the samples solution contains other oxidizing agents, e.g. digestion acids, it may be necessary to use more of the KI ascorbic acid reducing solution. As^{5+} may be measured with higher sensitivity if a longer reaction coil is used.

Bi FI-MHS Recommended Analytical Parameters for Bismuth

Parameters

Technique	AA
Wavelength	223.1 nm
Integration Time	15 sec.
Data Processing	Smoothing: 19 points
Cell Temperature	900 °C

Reagents

Carrier Solution	10% (v/v) HCl
Reducing Agent	0.2% $NaBH_4$ in 0.05% NaOH
Sample Solution	Bi^{3+} in 10% (v/v) HCl

Sensitivity Check

Analysis of 500 µL of a 10 µg/L bismuth solution should provide a signal of about 0.350 A. Data obtained using an EDL.

Notes

Samples to be analyzed for Bi should be prereduced by the addition of concentrated HCl. The reaction occurs immediately.

Hg1 FI-MHS Recommended Analytical Parameters for Mercury with $SnCl_2$

Parameters

Technique	AA
Wavelength	253.7 nm
Integration Time	20 sec.
Data Processing	Smoothing: 19 points
Cell Temperature	100 °C

Reagents

Carrier Solution	3% (v/v) HCl
Reducing Agent	1.1% $SnCl_2$ in 3% (v/v) HCl
Sample Solution	Hg^{2+} in acidified solution

Sensitivity Check

Analysis of 500 µL of a 10 µg/L mercury solution should provide a signal of about 0.1 A.

Notes

The flow of carrier gas should be increased to 70-100 mL/min to achieve quoted sensitivity.

Mercury sample and standard solutions should be stabilized by the addition of 1-2 drops of a 5% (w/v) $KMnO_4$ solution to 100 mL of solution.

The HCl acid concentration should be kept to a minimum to prevent the premature reduction of $KMnO_4$. Normally, 1 mL conc. HCl for 100 mL of sample reference solution is sufficient. Low mercury concentrations, < 10 µg/L, may be absorbed on the walls of the sample cups – this depends on the type of material used. The cups should be checked for their behavior.

If $KMnO_4$ is used for the Hg determination, it may lead to precipitation of MnO_2 on the walls of the cups. This results in low recovery values and is more prominent when cups are reused and not sufficiently cleaned.

Use of a longer stripping coil may give higher sensitivity.

Hg2 FI-MHS Recommended Analytical Parameters for Mercury with $NaBH_4$

Parameters

Technique	AA
Wavelength	253.7 nm
Integration Time	20 sec.
Data Processing	Smoothing: 19 points
Cell Temperature	100 °C

Reagents

Carrier Solution	3% (v/v) HCl
Reducing Agent	0.2% $NaBH_4$ in 0.05% NaOH
Sample Solution	Hg^{2+} in slightly acidified solution

Sensitivity Check

Analysis of 500 µL of a 10 µg/L mercury solution should provide a signal of about 0.07 A.

Notes

The flow of carrier should be increased to 70-100 mL/min to achieve quoted sensitivity.

Mercury sample and standard solutions should be stabilized by the addition of 1-2 drops of a 5% (w/v) $KMnO_4$ solution.

The HCl acid concentration should be kept to a minimum to prevent the premature reduction of $KMnO_4$. Normally, 1 mL conc. HCl for 100 mL of sample reference solution is sufficient. Low mercury concentrations, < 10 µg/L, may be adsorbed on the walls of the sample cups – this depends on the type of material used. The cups should be checked for their behavior.

Use of a longer stripping coil may give higher sensitivity. A lower concentration of the reductant (e.g. 0.02% (v/v) $NaBH_4$ in 0.005% NaOH) may reduce interferences and blank values.

Sb FI-MHS Recommended Analytical Parameters for Antimony

Parameters

Technique	AA
Wavelength	217.6 nm
Integration Time	15 sec.
Data Processing	Smoothing: 19 points
Cell Temperature	900 °C

Reagents

Carrier Solution	10% (v/v) HCl
Reducing Agent	0.2% $NaBH_4$ in 0.05% NaOH
Sample Solution	Sb^{3+} in 10% (v/v) HCl

Sensitivity Check

Analysis of 500 µL of a 10 µg/L antimony solution should provide a signal of about 0.2 A. Data obtained using an EDL.

Notes

Sensitivity can be improved by using a cell temperature of 1000 °C.

Samples to be analyzed for Sb should be prereduced prior to analysis.

To 10 mL of a neutral Sb^{5+} solution add 1 mL conc. HCl and 1 mL 5% (m/v) KI and 5% (m/v) ascorbic acid. The reduction occurs immediately.

Se FI-MHS Recommended Analytical Parameters for Selenium

Parameters

Technique	AA
Wavelength	196.0 nm
Integration Time	15 sec.
Data Processing	Smoothing: 19 points
Cell Temperature	900 °C

Reagents

Carrier Solution	10% (v/v) HCl
Reducing Agent	0.2% $NaBH_4$ in 0.05% NaOH
Sample Solution	Se^{4+} in 10% (v/v) HCl

Sensitivity Check

Analysis of 500 µL of a 10 µg/L selenium solution should provide a signal of about 0.200 A. Data obtained using an EDL.

Notes

The flow of carrier gas should be increased to 100-130 mL/min. Higher sensitivity can be obtained using a reaction loop 100 cm long with a 1 mm I.D.

Samples to be analyzed for Se should be prereduced prior to analysis by adding 1:1 conc. HCl to the sample or standard solutions followed by heating at 90 °C for 20 minutes. After prereduction, the solution may be diluted without the risk of "back oxidation" from Se^{4+} to Se^{6+}.

Sn FI-MHS Recommended Analytical Parameters for Tin

Parameters

Technique	AA
Wavelength	286.3 nm
Integration Time	15 sec.
Data Processing	Smoothing: 19 points
Cell Temperature	900 °C

Reagents

Carrier Solution	Saturated boric acid (approx. 50 g/L) in 1% (v/v) HCl
Reducing Agent	0.4% $NaBH_4$ in 0.05% NaOH
Sample Solution	Sn^{2+} or Sn^{4+} in saturated boric acid with 1% (v/v) HCl

Sensitivity Check

Analysis of 500 µL of a 10 µg/L tin solution should provide a signal of about 0.160 A. Data obtained using an EDL.

Notes

The carrier gas flow rate may be increased to 100 mL/min for better sensitivity.

If sensitivity decreases or memory effect occurs, condition quartz cell in 40% concentrated HF.

Samples and standards should have the same pH. Recommended value: pH 2-3. To obtain optimum sensitivities, the above mentioned solutions must be used.

Gas bubbles formed in the reduction solution are disturbing. Therefore use oNly a freshly prepared reducing solution which is stirred continuously by use of a magnetic stirrer.

Sensitivity can be improved by the use of argon with 1% oxygen.

Te FI-MHS Recommended Analytical Parameters for Tellurium

Parameters

Technique	AA
Wavelength	214.3 nm
Integration Time	15 sec.
Data Processing	Smoothing: 19 points
Cell Temperature	900 °C

Reagents

Carrier Solution	10% (v/v) HCl
Reducing Agent	0.2% $NaBH_4$ in 0.05% NaOH
Sample Solution	Te^{4+} in 10% (v/v) HCl

Sensitivity Check

Analysis of 500 µL of a 10 µg/L tellurium solution should provide a signal of about 0.350 A. Data obtained using an EDL.

Notes

Tellurium solutions should be prereduced prior to analysis by the addition of 1:1 conc. HCl and heating at 100 °C for 2 minutes.

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