

# Flow Injection Application Summary



# Flow Injection Application Summary

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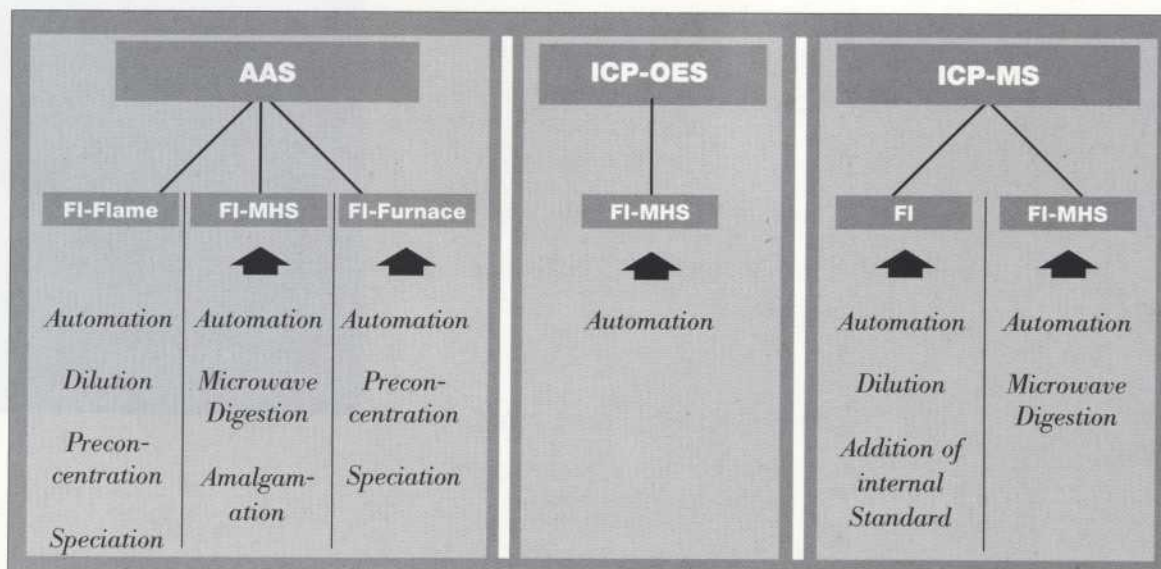
# Flow Injection - A Versatile Technique

Flow Injection (FI) is a technique that can be used ideally for the manipulation of sample and reagent streams in instrumental analysis. The purpose of this brochure is to provide you with fundamental descriptions and applications of the flow injection atomic spectroscopy techniques which have been carried out successfully so far.

## These techniques include:

- Automated hydride/cold vapor atomic absorption
- Automated amalgamation for mercury
- Automated on-line sample preparation using microwave digestion
- Analysis of solutions with high concentrations of dissolved solids with flame AA
- Automated on-line addition of buffers and modifiers
- Automated on-line dilution by mixing and/or dispersion
- On-line analyte preconcentration
- On-line species analysis
- Direct coupling of flow injection with graphite furnace AA
- Sample preparation and introduction for ICP-OES and ICP-MS
- On-line process control

Possible application areas for flow injection in atomic spectroscopy





# Flow Injection - A Convincing Principle

## Flow Injection Application Summary

### What is Flow Injection?

Flow Injection Analysis (FIA) was described initially by Ruzicka and Hansen [Anal.Chem. Acta, 1975, 78, 145]. A simplified explanation of the principle of the flow injection technique is as follows: A known, reproducible volume of a liquid sample is injected into a continuously flowing liquid (carrier) stream. The injected sample volume is transported by the carrier stream as a zone, which undergoes axial (longitudinal) and radial (lateral) dispersion processes, as well as chemical diffusion. If, at a suitable point, a reagent mixture is introduced into this system a reaction with the sample can take place during transport. As a result, each injected sample is subjected to the same physical and chemical processes.

Flow injection (FI) uses various sample and reagent flow configurations, which are tailored to the particular type of analysis performed, making it a versatile and flexible technique.

Flow injection provides automated sample preparation and introduction when used in conjunction with other analytical techniques such as atomic spectroscopy.

The significant advantages of flow injection atomic spectroscopy include:

- Fully automated analyses
- High sample throughput
- Low sample consumption
- Low reagent usage
- Reduced waste disposal costs.
- On-line sample pretreatment
- Absolute mass determinations
- Low memory effects
- Reduced risk of contamination
- Variable dynamic range by applying different sample volumes
- Fewer interferences

All important flow injection patents in most countries are owned and controlled by Bifok AB. Perkin-Elmer has the exclusive world-wide right to produce and sell flow injection products used in conjunction with atomic spectroscopy.

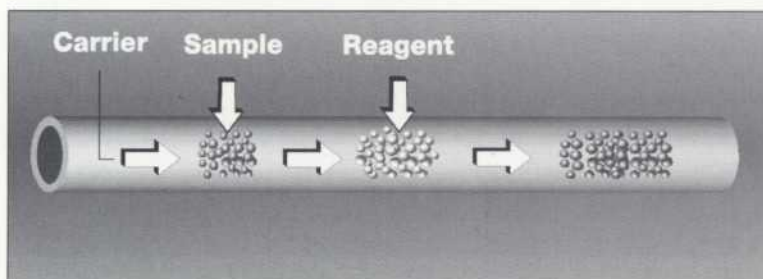
### Instrumentation

The Perkin-Elmer FIAS™ Flow Injection Systems, include one or two independently controlled peristaltic pumps for carrier, reagent and sample solutions. A FI switching valve and high quality FI components, such as tubing, connectors, and flow-merging hardware are also included. The easily replaceable sample loop is available in several sizes.

The peristaltic pumps use exchangeable tubing cassettes, which are precision-designed to secure pump tubing against the pump rollers, and are driven reproducibly by digital stepper motors. The tubing pressure for each cassette can be set by means of an easily accessible adjustment screw. Cassettes containing single or double tubing sets (for larger or smaller diameter tubing, respectively) can be used. Pump speed can be programmed with the system software.

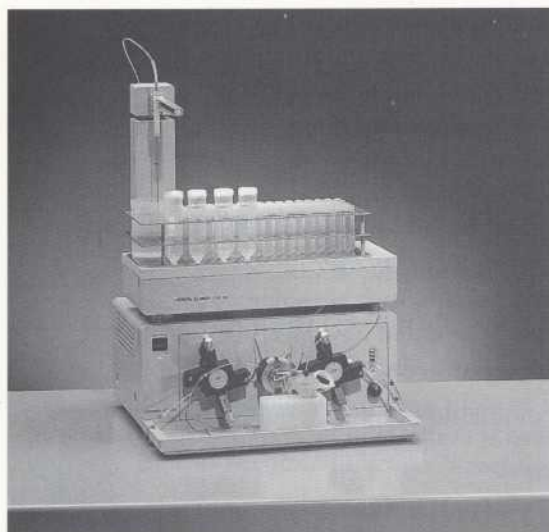
The modular design of the manifold section offers high flexibility for different applications. Each supplied manifold block has two inlet channels for merging flows, and one for outlet.

For automatic sample introduction the Perkin-Elmer AS-90 or AS-91 Autosampler can be connected.

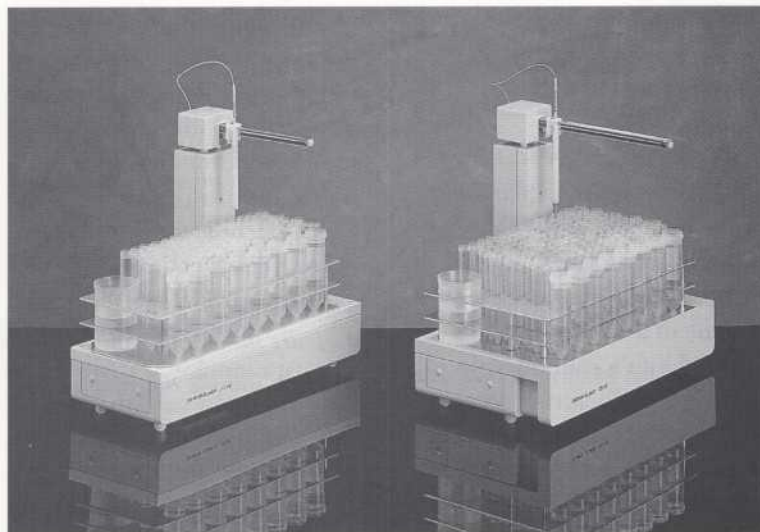


Simplified principle of flow injection techniques

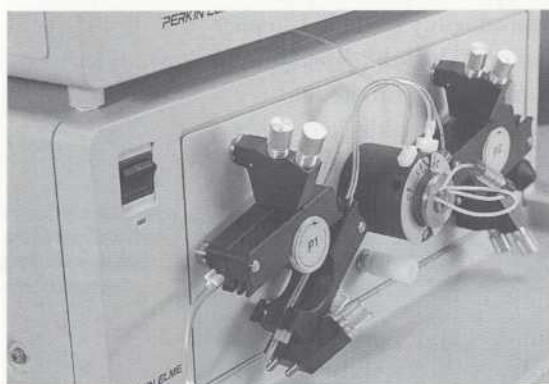
# Flow Injection - A Convincing Principle



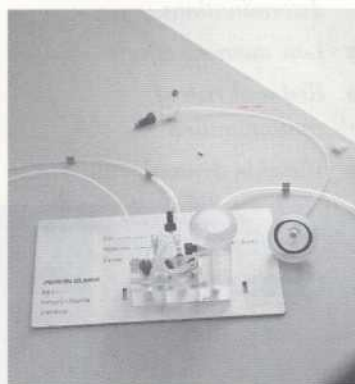
The Perkin-Elmer FIAS-400 Flow Injection System



For automatic sample introduction the Perkin-Elmer AS-90 or AS-91 Autosampler can be connected.



FI Switching Valve and Peristaltic Pumps



Mixing Section

# General Description

The coupling of flow injection with flame AA extends the range of application for flame AA significantly. Flow Injection-Flame Atomic Absorption (FI-FAA) operation is also fully automated, permitting automatic sequential multi-element analyses with appropriate AA instruments.

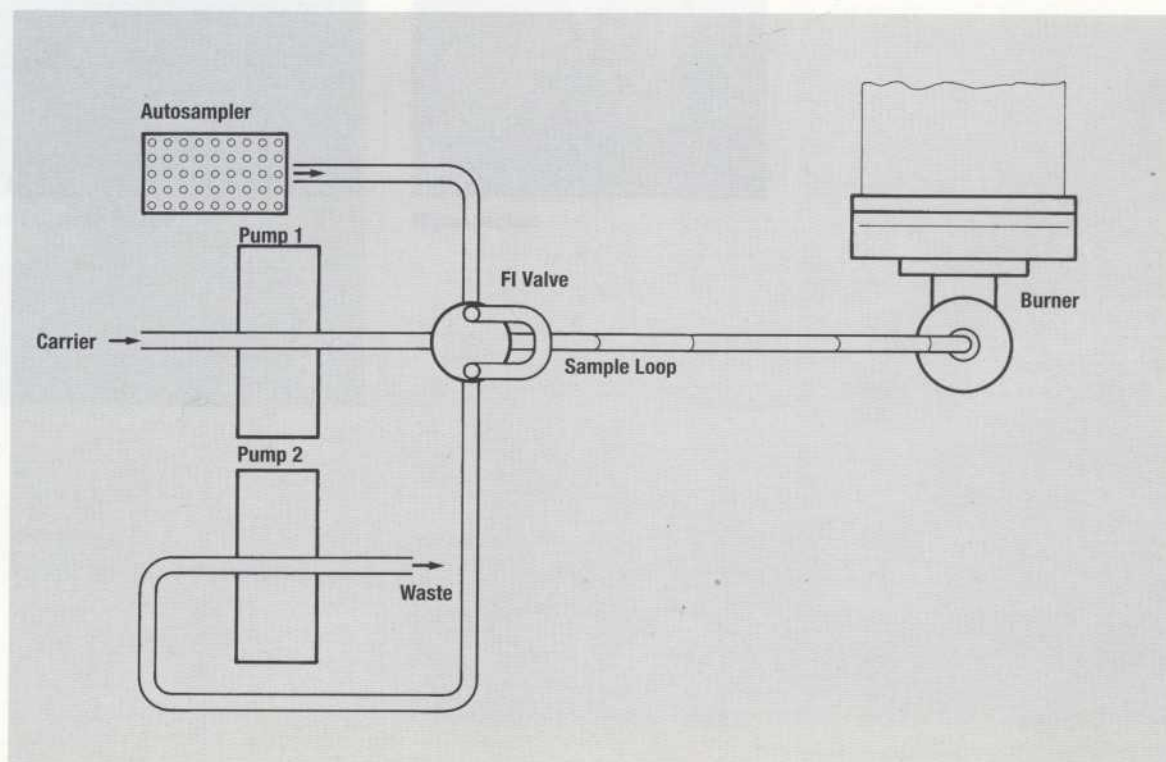
## FI-FAA is the preferred technique for:

- Automated on-line dilution by reproducibly controlled dispersion
- The analysis of samples containing high levels of dissolved solids
- The analysis of reduced sample volumes
- Automated on-line addition of buffers and modifiers, i.e. ionization suppressants.
- On-line species analysis
- Automated on-line preconcentration

## Principle of Operation

In this mode the FI functions as shown in the figure below. The carrier stream (e.g. deionized water, dilute acid) is continuously transported by means of the peristaltic pump P1. The FI-valve is electronically switched between FILL and INJECTION. In position FILL the sample loop is filled using peristaltic pump P2. The FI-valve is now switched to position INJECTION, and the exact and reproducible volume of sample contained in the loop is introduced into the carrier stream and transported directly into the nebulizer of the AA instrument. This FI operating mode is also fully automated permitting sequential multi-element analysis.

Flow schematics of FI-Flame AA.





# On-line Dilution

One of the simplest and most common uses of flow injection is mixing the analyte solution with streams of other liquids. These other liquids may be solvents for diluting the sample or reagents, such as ionization buffers for the determination of alkali metals by flame AAS.

A wide range of solution ratios is available merely by varying the tubing diameters and pumping rates. Mixing

occurs either in a Y-connector, a mixing coil, or a mixing block.

There are fundamentally two basic modes of operation for dilutions and the addition of solutions using the FIAS. The liquid streams simply may be mixed and transported to the nebulizer, or the mixing process may be combined with flow injection.

## On-line Dilution without Flow Injection

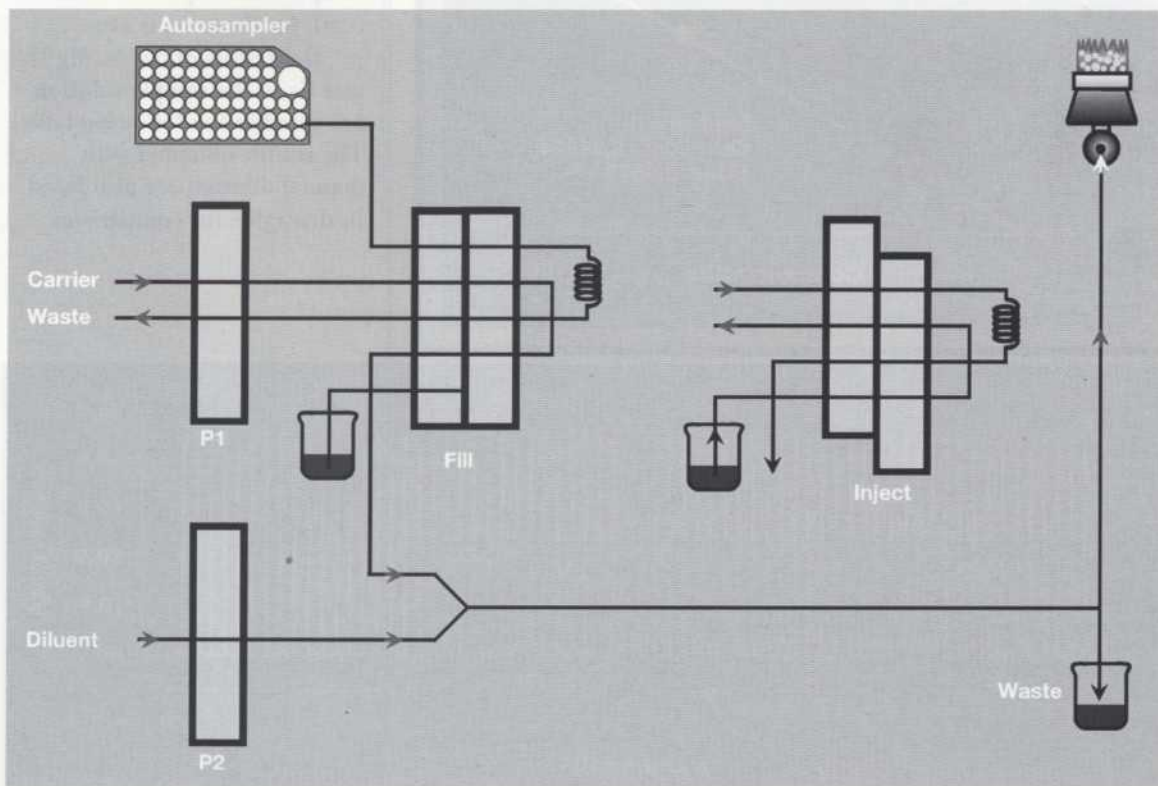
The dilution of sample solutions for analysis by flame AAS may be necessary to

reduce the sensitivity of the method when other means, such as choosing a secondary line, are unsuitable, or to reduce certain types of interferences which occur with concentrated samples.

## Dilution with Flow Injection

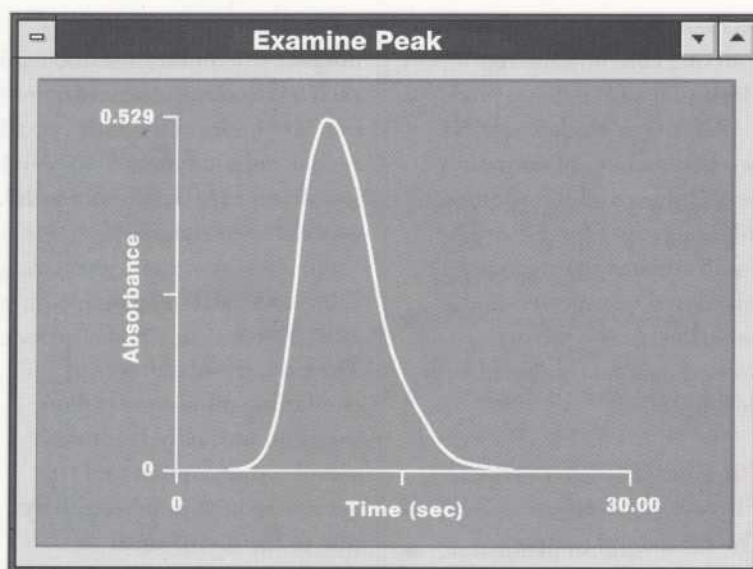
The primary advantages of combining dilution with flow injection normally are lower sample consumption and greater reduction in sensitivity due to the use of small injection volumes. The FIAS configuration used for such a system is shown below.

Configuration of the FIAS used as an automatic dilution apparatus

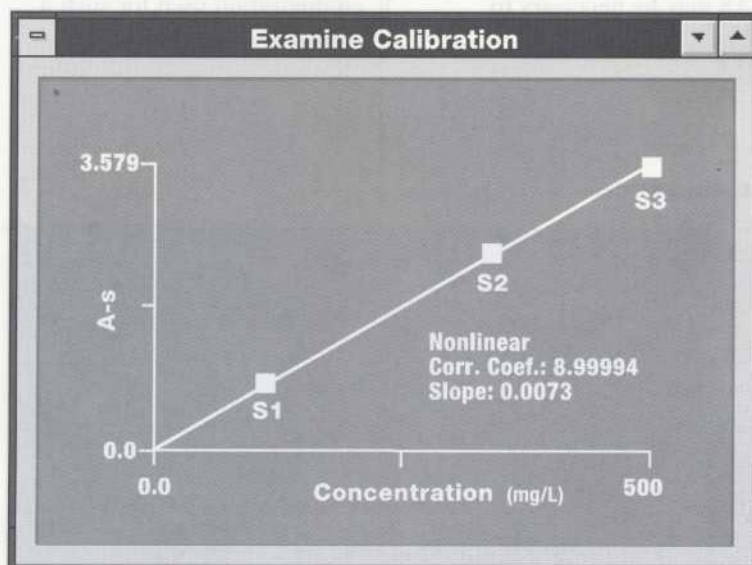


# On-line Dilution

Signal trace of  
Mg in acid  
concentrate



Calibration Curve of  
Mg for FI-Flame AA  
with on-line  
Dilution. Standard  
Series: 100, 300,  
500 mg/L Mg.



## Determination of Na, K, Mg, Ca in Acid Concentrate

In this example the four elements Na, K, Mg and Ca in acid concentrate used for dialysis purposes were measured directly with flame AA after on-line dilution by flow injection. The concentrations in the sample were 64,000 mg/L Na, 450 mg/L Mg, 2,000 mg/L Ca and 1,400 mg/L K. The measured results were compared with conventional flame AA and manual dilution. Good agreement was found between the two methods.

The RSD values of the measured elements in the sample were about 2% at a dilution factor of 1000. The sample consumption was about 5 mL for three replicates.

The results of Na, K, Mg and Ca in the sample solution are listed in the following table. The results obtained with manual dilution are also listed in that table for comparison.

Elements	Na (mg/L)	K (mg/L)	Mg (mg/L)	Ca (mg/L)
FIAS Automatic Dilution	64413 ± 309 n = 4	1430 ± 38 n = 7	458 ± 5 n = 9	2046 ± 25 n = 7
Manual Dilution	64525 ± 303 n = 8	1450 ± 6 n = 3	459 ± 1 n = 5	2030 ± 26 n = 5



# Direct Analysis of Highly Concentrated Matrices

FI-Flame AA is ideally suited to the automated analysis of samples containing high concentrations of dissolved solids. For example, saturated salt solutions can be directly analysed over an extended period. There is reduced danger of blocking the burner or the nebulizer since the system is thoroughly rinsed with the carrier stream solution after each measurement. This continuous rinsing of the burner/nebulizer system with aerosol prevents drying processes and chemical reactions between the matrix and air, avoiding matrix deposits. The constantly alternating aspiration of solvent and air is eliminated, so the stability of the flame is also improved.

## Analysis of Salt Solutions

By using FI-FAA, it is possible to analyze samples containing up to 30% NaCl over extended periods of time without clogging the burner head or nebulizer. As an example, the results from the analysis of solutions containing 2 mg/L copper and various NaCl concentrations are shown in the table and figure below. A 390- $\mu$ L sample loop was used.

NaCl wt (%)	No. of Replicates	RSD (%)
15	60	3.3
20	33	4.5
20	11 x 7 sets	1.7*
30	11 x 4 sets	3.1*

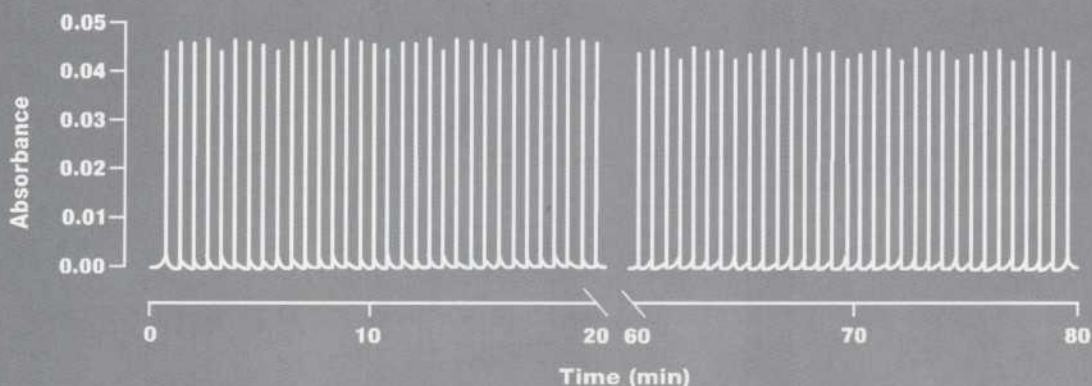
\*The nebulizer was adjusted with the test solution for optimum signal:noise ratio prior to these reproducibility tests.

## Determination of Ti in Aluminum Alloys

The following table shows analytical results obtained using FI-FAA for the determination of Ti in aluminum alloys. No burner head clogging was noted with the FI-FAA determinations; however, the burner head clogged in about 2 minutes using continuous aspiration and a nitrous oxide-acetylene flame.

Measurements were made using reference alloys from the Federal Institute for Material Testing (BAM), Berlin-Dahlem. Approximately 5 g of the alloy was dissolved in hydrochloric acid and diluted to 100 mL. The method of additions was used to correct for transport-type interferences.

Al Alloy	Measured Ti Content wt (%)	Certified Ti Content wt (%)
BAM 202	0.034	0.03
BAM 206	0.016	0.013
BAM 300	0.014	0.012
BAM 304	0.016	0.015



By using FI-FAA, it is possible to analyze samples containing 30% NaCl over extended periods of time without clogging the burner or nebulizer

# Direct Analysis of Highly Concentrated Matrices

## Determination of Zn and Mn in Wheat Flour

Approximately 1 g of wheat flour was dissolved in 5 mL of concentrated nitric acid and 3 mL of water at 160 °C in an autoclave. The solution was diluted to 25 mL. A 390- $\mu$ L sample loop was used.

NBS 1576 Wheat Flour	Measured Content ( $\mu$ g/g)	Certified Content ( $\mu$ g/g)
Mn	$8.2 \pm 0.1$	$8.5 \pm 0.5$
Zn	$10.0 \pm 0.1$	$10.6 \pm 1.0$

## Determination of Cr in Steel

Approximately 1 to 2.5 g of steel were dissolved in 1:1 hydrochloric acid and a few drops of nitric acid. The solutions were diluted to 100 mL, except for those with high chromium content which were diluted to 200 mL. The measurements were made using a nitrous oxide-acetylene flame, and the results were calculated based on calibration with aqueous standard solutions. A 390- $\mu$ L sampling loop was used.

Steel	Measured Cr Content (wt %)	Certified Cr Content (wt %)
BAM 4b/2330	$0.038 \pm 0.002$	$0.040 \pm 0.003$
BAM SiMn 1/970	$0.201 \pm 0.002$	$0.193 \pm 0.008$

## Plating Baths

The determination of aluminium in plating baths is a problem due to the high salt content of the solutions. The sample analyzed was a nickel plating bath containing 120 g/L nickel and over 30% total dissolved solids. Using continuous aspiration, the nitrous oxide burner head slot clogged very quickly. Using flow injection flame AA with a 150- $\mu$ L sample loop, the aspiration of the sample solution was free of problems.

Measurement No.	Al (mg/L)	Std. Dev.
1	5.8	0.3
2	5.8	0.5
3	6.2	0.4
4	5.9	0.2

3 replicates

## Gold in Extraction Solutions

The gold extracts analyzed contained approximately 10% thiourea, 3% sulfuric acid, and 1% other salts. A 10-g sample weight, either a 60-mL or an 80-mL extract volume, and a 390- $\mu$ L sample loop were used for the determinations.

Extract	FI-FAA	Fire Assay
Au (g/t)	14.6*	14.8
Std. Dev.	0.7	—
RSD	4.9 %	—

\*Average of nine separate extractions

The FI-FAA results agreed very well with the results obtained using the classical, considerably more time-consuming fire assay method.



# On-line Reagent Addition

## Automated Addition of Reagents

It is often necessary to add reagents to the analyte solution in order to reduce interferences with flame AAS. Well known examples are the addition of lanthanum or strontium to calcium solutions to avoid chemical interferences by phosphate, and the reduction of ionization interference in the determination of potassium by the addition of cesium chloride.

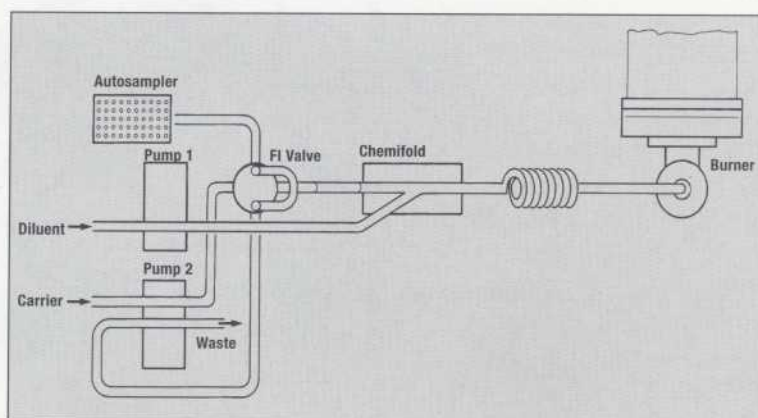
The addition of a reagent using the FIAS is similar to the dilution procedure, only reagent solution is added instead of diluent. The solution ratios typically will be somewhat different than for automatic dilution since, in many cases, sample dilution must be kept to a minimum. In general, a small amount of reagent is added to a relatively large amount of sample. On-line sample dilution and addition of a reagent may even be combined with the FIAS. The determination of alkaline elements, for example, usually require both dilution and addition of a buffer.

## Addition of Cesium Chloride as an Ionization Buffer

The addition of cesium chloride or other alkali metal salts is essential in flame AAS to avoid ionization of alkali metals, alkaline-earths, and other elements. This can be done automatically with the FIAS. Analytical results obtained using the automated addition of cesium chloride buffer during the determination of potassium in certified standard materials are shown in the table below.

Sample	% Potassium	
	Measured	Certified
Orchard Leaves	$1.45 \pm 0.01$	$1.47 \pm 0.03$
Bovine Liver	$1.05 \pm 0.04$	$0.97 \pm 0.06$

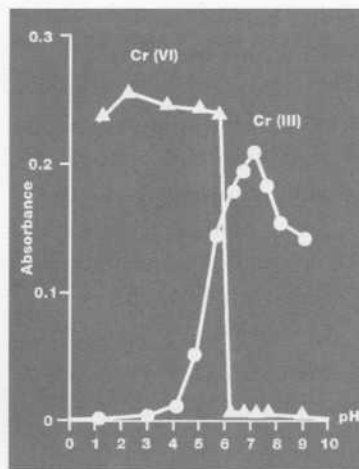
There are advantages for the analyst in using the FIAS rather than manually adding cesium chloride. Aside from a considerable time savings during sample preparation, less reagent is used since it is added only to the portion of sample solution which is actually used for the measurement. Also, only a small amount of sample is required. Sensitivity can be controlled by the choice of sample loop, pump tubing diameters, and pumping rates. Although the determination is not as rapid as conventional flame AAS, the combined analysis time including sample preparation compares favorably and, of course, the analysis is automated.



Schematic diagram of the FIAS configured for the addition of cesium chloride.



sensitivity enhancement of 25 for a 3-mL sample loading. The effect of concomitant species was investigated, and satisfactory recovery of 90 to 106% could be obtained from natural water samples. For a preconcentration time of 30 sec. a linear calibration for both species was established over the concentration range 10 to 200  $\mu\text{g/L}$  with detection limits ( $3\sigma$ ) of 1.0 and 0.8  $\mu\text{g/L}$  for  $\text{Cr}^{3+}$  and  $\text{Cr}^{6+}$ , respectively.



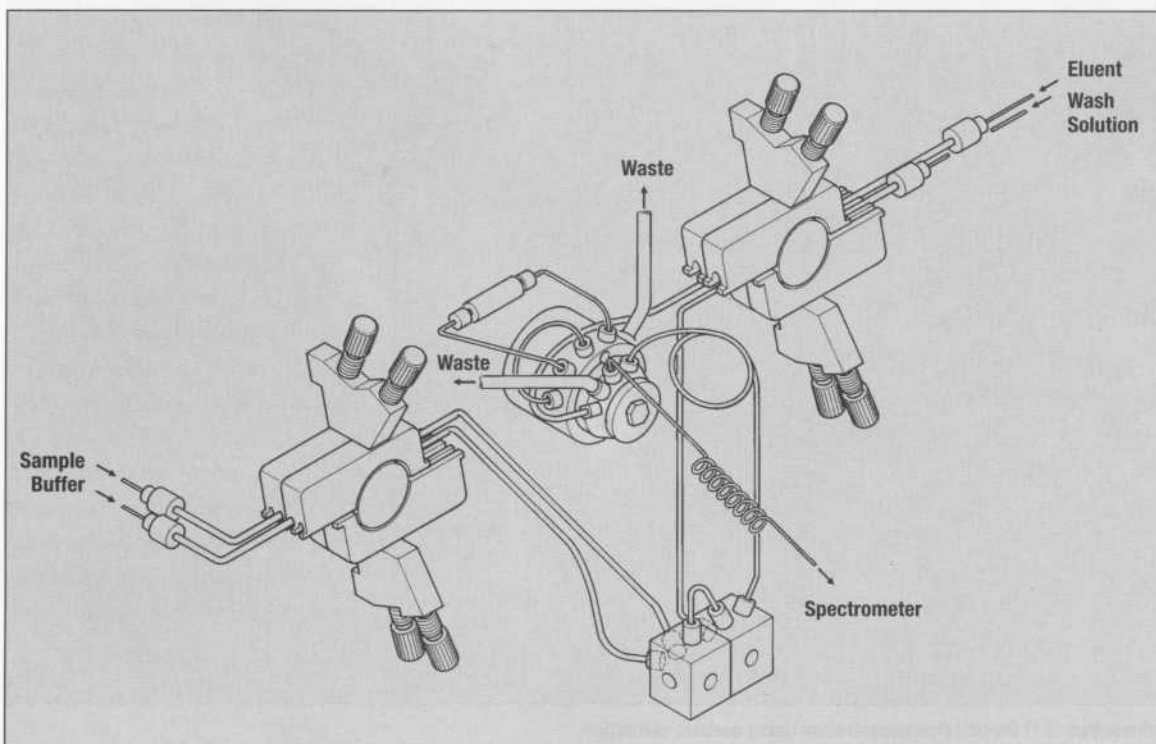
Preconcentration efficiency = f (pH) of the buffer solution

## Performance Data

	$\text{Cr}^{3+}$	$\text{Cr}^{6+}$
Working range ( $\mu\text{g/L}$ )	10–200	10–200
Sensitivity enhancement (EF)	25	25
Conc. efficiency (EF/min)	23	23
Char. conc. ( $\mu\text{g/L}$ , peak height)	3.9	3.2
Detection limit ( $\mu\text{g/L}$ )	1.0	0.8
Sample consumption (mL)	3.0	3.0
Measurements / hour	55	55

## Analytical results

Sample	Certificate [ $\mu\text{g/L}$ ]	Found [ $\mu\text{g/L}$ ]	
		$\text{Cr}^{3+}$	$\text{Cr}^{6+}$
NIST-1643b	$18.6 \pm 0.4$	$18.0 \pm 0.5$	nd
NIST-1643c	$19.0 \pm 0.6$	$19.5 \pm 0.5$	nd



Tubing Diagram for On-line Species Determination

# On-line Analyte Preconcentration

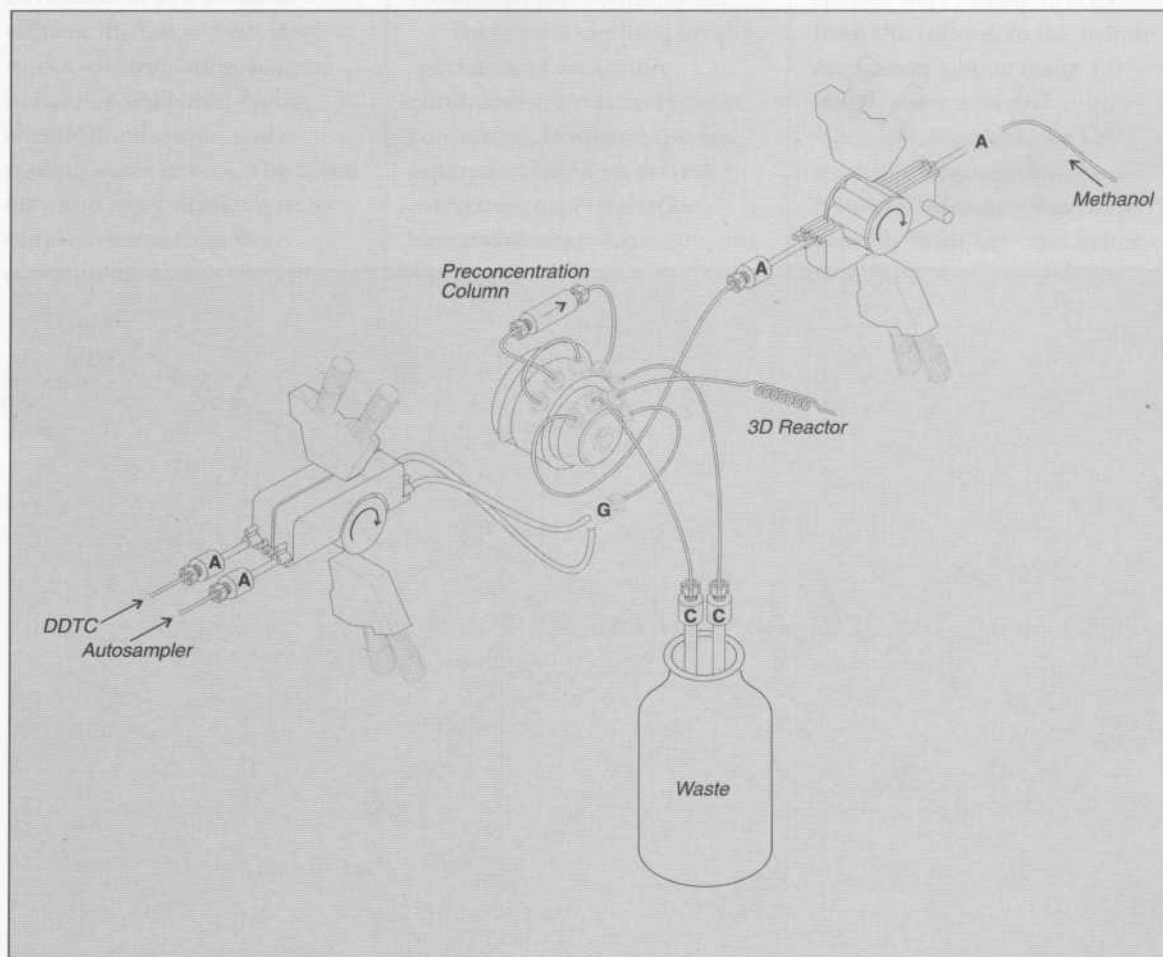
With many sample types, the analyte concentration can be too low for direct determination by flame atomic absorption. Frequently, time-consuming sample preparation techniques are required to extract or preconcentrate the elements of interest. With the Perkin-Elmer On-line Preconcentration Kit for the FIAS, such procedures can now be fully automated using advanced flow injection

techniques. On-line preconcentration of trace elements enhances the detection limits of flame atomic absorption, extending the fields of application significantly.

Some of the key benefits you can obtain with the On-line Preconcentration Kit for the FIAS include:

- *Analyte preconcentration for improved detection limits in your sample matrices.*

- *Complete, computer-controlled automation for operational simplicity.*
- *Significantly reduced sample preparation time.*
- *Reduced risk of contamination during sample preparation*
- *Improved accuracy by separating potentially interfering matrix components prior to the analytical measurement.*



Schematics of FI On-line Preconcentration using sorbent extraction

Two different preconcentration techniques are currently offered:

### 1. Preconcentration with Sorbent Extraction

The most commonly used method is on-line preconcentration with sorbent extraction. The sample is mixed automatically with a chelating agent and passed to a specially designed column containing C18-coated silica or other sorbent materials. After the desired preconcentration time, adsorbed metal chelates are eluted with alcohol and transported to the flame via the nebulizer. All steps, including sampling, mixing, preconcentration on the column and elution, are fully automated and controlled by the AA instrument's computer.

With proper selection of a suitable chelating agent column material and eluent, this technique provides very selective preconcentration of specific metals such as Cu, Cd, and Pb. This allows them to be separated from undesirable matrix components, such as high concentrations of alkali metal or alkaline earth salts. For example, using automated on-line preconcentration, these elements have been successfully determined directly in drinking water, coastal seawater and mining effluents using flame atomic absorption.

Sensitivity enhancement for several elements preconcentration time 60 s.

Element	Concentration (mg/L)	Sensitivity Enhancement
Ag	0.01	135
Al	6.0	—
As	2.0	174
Au	0.04	135
Bi	0.2	81
Cd	0.005	70
Co	0.01	73
Cr	1.0	—
Cu	0.05	50
Fe	0.2	14
Mn	0.5	—
Mo	0.1	142
Ni	0.04	72
Pb	0.05	60
Pd	0.005	107
Pt	20.0	—
Se	0.2	155
Sn	5.0	—
Ti	10.0	—
Tl	0.5	—
V	10.0	—
W	2.0	106
Zn	0.01	36

### Determination of Pb, Cd, and Cu in NIST 1643b Water

The characteristic concentration for the determination of lead using flame AAS with a flow spoiler is 0.19 mg/L. The lead concentration in the NIST 1643b water sample is 0.027 mg/L. To obtain a sufficiently large enrichment factor a 60 second preconcentration time was applied. For the determination of cadmium and copper, 20 seconds are sufficient. The analytical results obtained are shown in Table below.

Element	Measured [µg/L]	Certified [µg/L]
Lead	23.0 ± 0.4	23.7 ± 0.7
Cadmium	19.0 ± 0.3	20.0 ± 1.0
Copper	22.0 ± 0.4	22.3 ± 0.4



## Determination of Pb and Cd in Sea Water

The recoveries for lead and cadmium in synthetic sea water samples were determined to be at or near 100%. Recoveries were lower in strongly acid solutions. For cadmium, the pH of the solution must be at least 2.0 to obtain 98% recovery, whereas for lead, recoveries of 100% were obtained even at pH 1. The experimental parameters used are listed in the table below.

Parameter	Lead	Cadmium
Concentration, $\mu\text{g/L}$	20	10
Recovery, %	100	98
Absorbance	0.046	0.040
Enrichment Factor	100x	25x
Enrichment Time, s	60	20

## Determination of Trace Elements in Mining Effluent

Solid content:

Sample A: 3%

Sample B: 10%

Method checked by:

- Method of addition
- Dilution of sample
- Change of preconcentration time
- Comparison of peak shapes

Element	Content ( $\mu\text{g/L}$ )		D.L. ( $\mu\text{g/L}$ )	Preconc. Time (s)
	Sample A	Sample B		
Cd	0.9	3.0	0.07	40
Co	2.5	67.5	1.1	30
Cu	4.6	8.8	0.2	40
Ni	10.0	135	0.5	30
Pb	0.6	1.9	0.1	60

## Determination of Pb and Cd in Drinking Water

The recoveries for lead and cadmium in drinking water were determined using the same analytical conditions as for sea water. Recoveries for both lead and cadmium were 100 %. The table below lists all data pertinent to the analysis.

Parameter	Lead			Cadmium		
	0	10	30	0	1	3
Conc., $\mu\text{g/L}$	0	10	30	0	1	3
Abs.	0.005	0.027	0.073	0.006	0.012	0.033
Enrichment	100x			25x		
Time, s	60			20		
D.L., $\mu\text{g/L}$	3			0.3		
FDR*	40			5		
USEPA*	20			10		

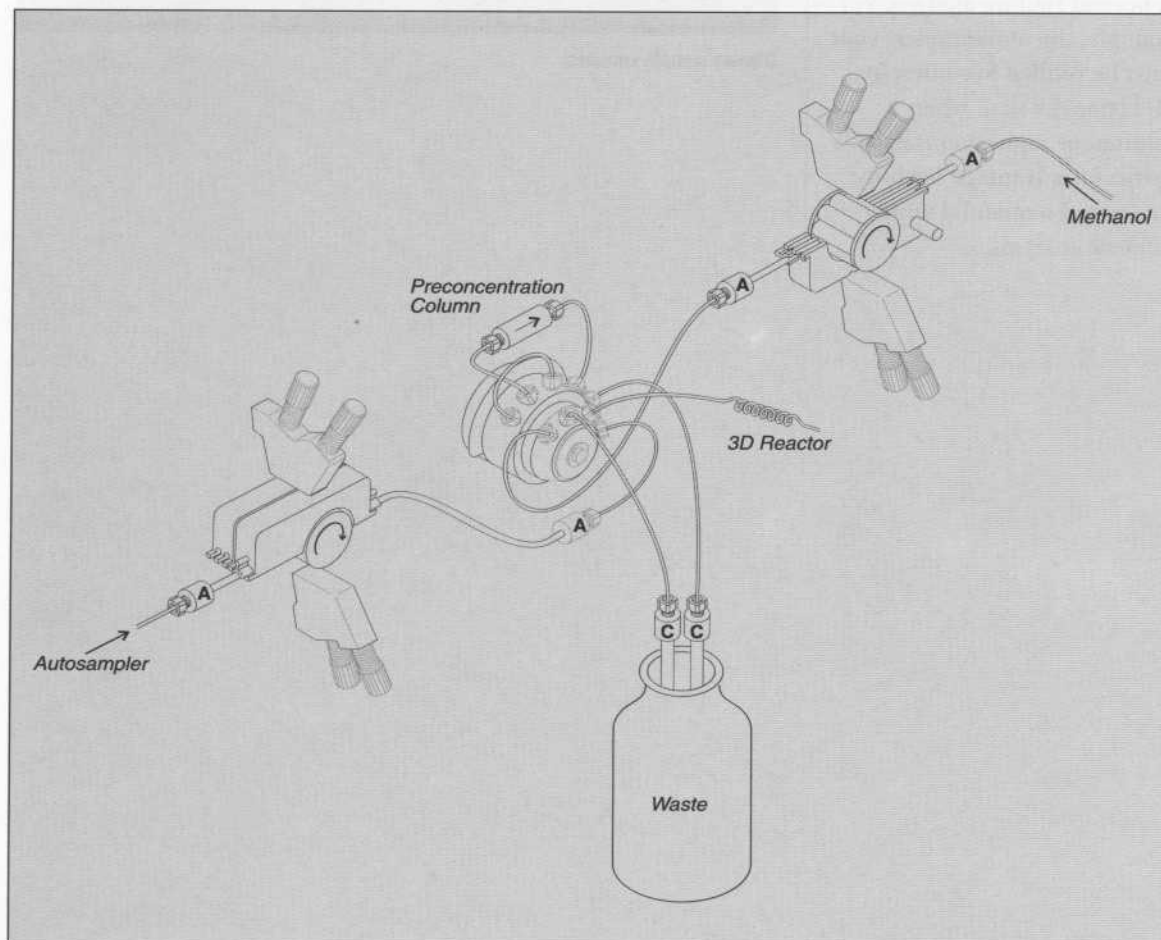
\*USEPA = United Status Environmental Protection Agency

## 2. Preconcentration by Ion Exchange

Ion exchange is another proven method for the FIAS automated preconcentration system. For example, this technique has been used for the determination of gold in ores using an XAD-8 column. A preconcentration factor of 15-20 can easily be obtained with a preconcentration time of only

20 seconds. This improves the flame AA detection limit for gold in ore to approximately  $2.0 \mu\text{g/L}$ .

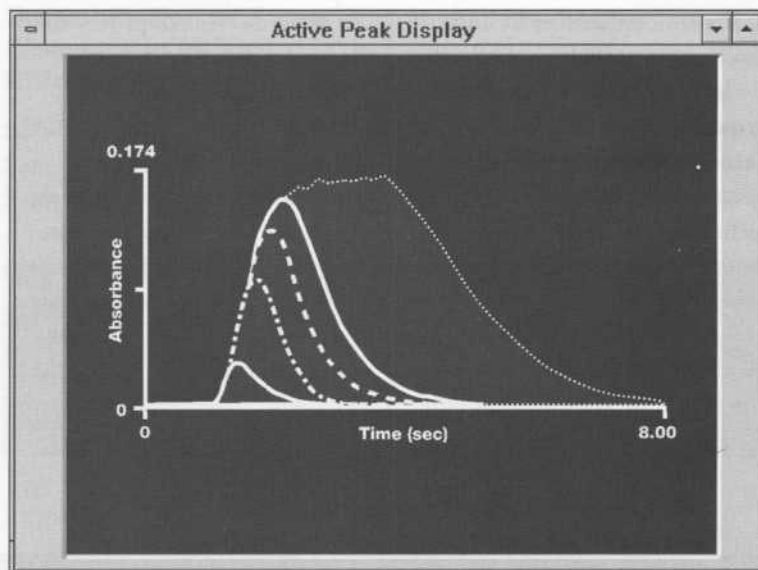
Automatic on-line preconcentration saves sample preparation and analysis time and costs. It also enhances sample throughput and reduces the potential for interferences for better analytical accuracy.



Schematics of FI on-line Preconcentration using ion exchange

# Reduced Sample Volumes

Sample consumption is much less with FI-Flame AA than with conventional Flame AA and continuous aspiration. Since a total of 800 - 1000  $\mu\text{L}$  are required for a determination, FI-Flame AA is advantageous when samples are available only in small quantities or are costly, as is the case for material from living organisms, expensive pharmaceutical products or noble metals. Low sample consumption is also of benefit in normal routine analysis. For example, the autosampler vials must be refilled less often for FI-Flame AA than when continuous aspiration is used, a particular advantage for fully automated sequential multi-element analyses.



Display sample volumes



# Literature for FI-Flame AA

## Flow Injection Application Summary

Element	Matrix	Perkin-Elmer Lit. No.
Cr (Speciation)	Water	AS-1221
Ca	Phosphat	AS-1211
Cu	High diss. Matrix	AS-1212
Cd, Cu, Pb,	Sea Water, Preconcentr.	AS-1213
Pb	Biol. samples, Preconcentr.	AS-1215
Cd, Cu, Pb,	Water, Preconcentr.	AS-1214
Cd, Co, Ni	Biol. samples, Preconcentr.	AS-1216
General	Automated Dilution	TSAA-16
General	Automated Preconcentration	TSAA-15
General	High Dissolved Solids	TSAA-11
General	High Dissolved Solids	AS-1137
General	Optimization of Parameters	AS-1136

# Flow Injection Application Summary

## Part 3: Flow Injection Mercury/Hydride AA

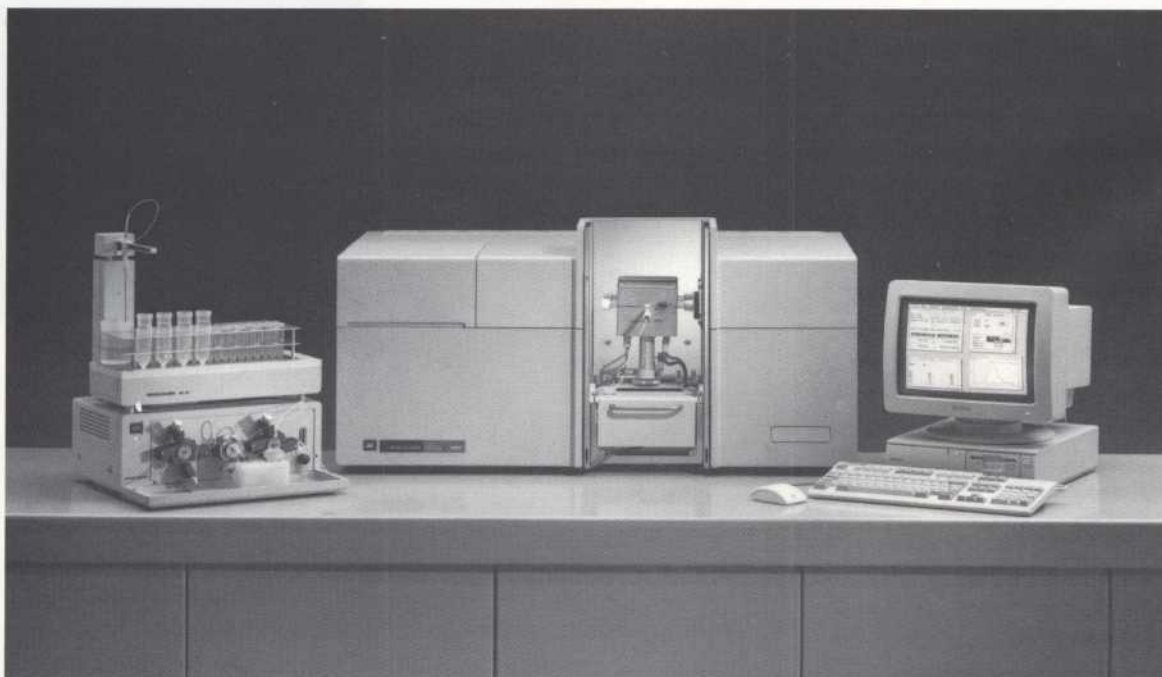
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Determination of Total Hg in Environmental Samples with FI/MDS	40
Literature for FI-MH AA	41

# Flow Injection Mercury/Hydride AA

**The main advantages of flow injection mercury/hydride atomic absorption (FI-MH) are:**

- Fully automated operation.
- High analysis speed; up to 2 determinations per minute.
- Same relative detection limits (D.L.) as with batch systems, but a factor of 50 to 100 better absolute D.L.
- Very low sample consumption;  $< 500 \mu\text{L}$  per determination with excellent detection limit.
- Low reagent consumption.
- Very cost efficient.
- Fully automated dedicated flow injection mercury system (FIMS<sup>TM</sup>) also available.
- Highest sensitivity for Hg by use of the automated amalgamation technique.





# FI-MH – Flexible and Cost-effective

## Manual Mercury/Hydride Atomic Absorption

For many years the cold vapor mercury and hydride generation techniques have been successfully used in conjunction with atomic absorption for the very sensitive, selective determination of mercury and the elements which form gaseous hydrides, such as As, Se, Sb, Te, Bi and Sn.

Before analysis the sample is prepared in such a way that the elements of interest are in ionic form in solution. Introduction of a reducing agent ( $\text{NaBH}_4$  or  $\text{SnCl}_2$  for Hg) into the sample causes a reaction which produces the gaseous hydrides or reduces mercury to the elemental form. A carrier gas stream transports the hydrides (or mercury) into a heated quartz cell mounted in the measurement beam of an atomic absorption spectrometer. The hydride in the cell decomposes on heating and the amount of the analyte element is then measured by atomic absorption spectroscopy.

The principle of separation of the analyte metals from interfering matrices is a major advantage of mercury/hydride techniques. Therefore matrix interferences and background absorption are very rare with these techniques.

Mercury/hydride systems have been commercially available for atomic absorption since 1965. With these accessories mercury/hydride techniques are applied manually or semi-automated in a batch

mode. The lack of automation and the relatively large sample, reagent and time consumption required for a determination are the major limitations of these systems.

## Fully Automated Flow Injection Mercury/Hydride AA

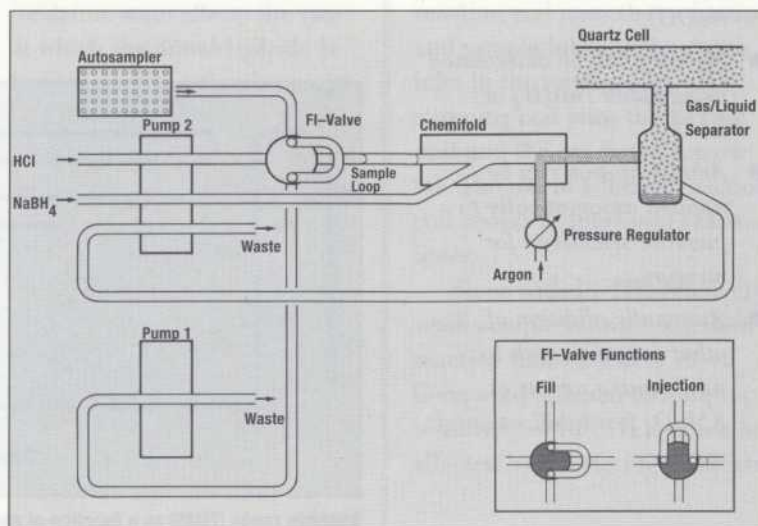
The principle of operation of the Perkin-Elmer flow injection systems (FIAS) for FI mercury/hydride AA is shown in the flow diagram below and can be described as follows:

The first channel of the peristaltic pump, P2, propels the acidified carrier stream. The FI valve is switched electronically to positions FILL or INJECTION. In the FILL position the sample loop is filled with sample by pump P1. The FI valve then switches to INJECTION, and an exact and reproducible sample volume is

introduced into the carrier stream from the sample loop.

The second channel of pump P2 transports the reducing agent  $\text{NaBH}_4$  (or  $\text{SnCl}_2$  for Hg) to the mixing section (reaction cell and manifold). As soon as the sample volume reaches this point, it mixes thoroughly with the reducing agent and a spontaneous reaction occurs in which the gaseous hydride of the analyte element is generated during the reaction, or mercury is reduced to the elemental form. The hydrogen which is released and an additional stream of argon transport the hydride or Hg into the quartz cell mounted in the measurement beam of the atomic absorption spectrometer. The liquid which is separated from the gas is drawn off by means of the third channel of pump P2 and pumped to waste.

FI-MH Flow Diagram.



# FI-MH – Best Analytical Performance

## FI-MH is very flexible and easy to handle:

- To optimize analytical performance, the tube dimensions and pump speeds may be changed. For routine operation the same tube dimensions and pump speed can be used for all elements.
- Different sample volumes may be used to influence sensitivity or to overcome interferences. For routine analyses the same sample volume is used for all elements.
- Additional tubings (reaction coils) may be used for special applications, such as analyte pre-reduction from higher to lower oxidation states.
- The same carrier solution (3% HCl) can be used for all elements except Sn, which requires boric acid + HCl.
- The same reductant solution can be used for all elements (0.2% NaBH<sub>4</sub>, 0.05% NaOH).
- Mercury can be determined using either NaBH<sub>4</sub> or SnCl<sub>2</sub>.
- Amalgamation can be applied automatically to increase sensitivity for mercury.
- Automatic addition of other reagents, such as antifoaming agents or KMnO<sub>4</sub> for stabilization of mercury.

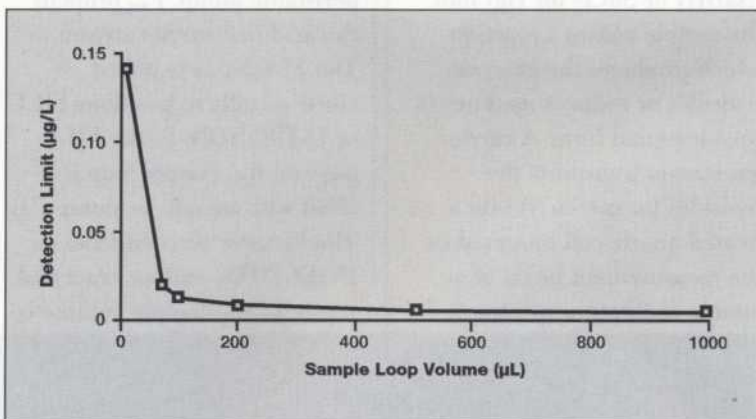
Comparison of flow injection mercury/hydride AA with batch and continuous flow techniques

	FI-MH System	Batch System	Cont. Flow System
Simple instrumentation	+	+	+
No spectral interferences	+	+	+
Control of chemical interferences	+	+	-
Good reproducibility	++	+	+
High relative sensitivity	+	+	-
High absolute sensitivity	++	-	-
Small sample volumes	++	-	-
Easy automation	+	-	+
High sample throughput	++	-	-
Variable sample volumes	++	+	-

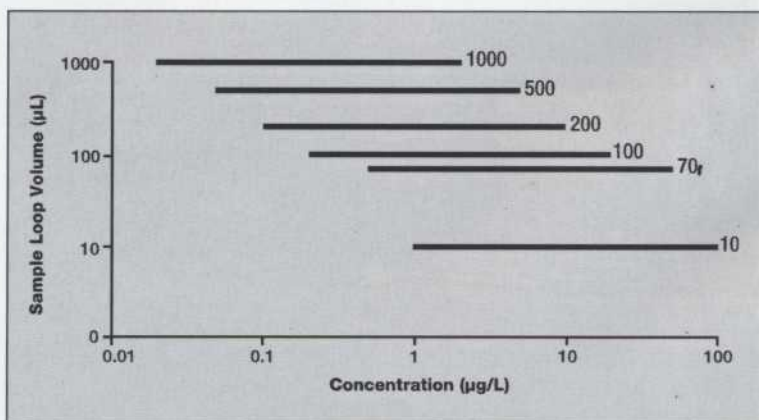
+ = good

++ = very good

- = poor



Detection limit as function of sample loop volume (FIMS)



Dynamic range (FIMS) as a function of sample loop volume



# FI-MH – Wide Range of Applications

## Consumption and cost comparison

	FIAS	Batch	Cont. Flow
Sample (mL)	1.0	1.0	8
conc. HCl (mL)	0.5	0.5	1
NaBH <sub>4</sub> (mg)	5	200	6
NaOH (mg)	1	70	5
relative cost	1	12	1.8
Time (seconds)	40	100	60

## Sensitivity

Relative or solution sensitivity ( $\mu\text{g/L}$  of analyte to produce a signal of 0.0044 A) for FI-MH is comparable with that obtained using other mercury/hydride techniques. Because FI-MH requires much smaller sample sizes, however, the absolute sensitivity (nanograms of analyte to produce a signal of 0.0044 A) attainable is significantly better than for most other mercury/hydride techniques, implying smaller sample requirements.

With flow injection the sensitivity of the analysis depends on the amount of sample used, which is determined by the size of the sample loop located on the injection valve. A typical analysis with FI-MH uses 500  $\mu\text{L}$  of sample.

Another factor that can affect the sensitivity is the oxidation state of the analyte. In solution, arsenic, selenium, antimony, bismuth and tellurium can exist in two or more different oxidation states. The oxidation state affects the rate at which the metal-hydride is formed and thus the sensitivity.

## Relative Sensitivities

500  $\mu\text{L}$  of 10  $\mu\text{g/L}$  solution typically will give the following absorbance values

As	0.450
Bi	0.470
Sb	0.200
Se	0.100
Sn	0.160
Te	0.370
Hg	0.070
(with SnCl <sub>2</sub> : 0.100)	1 $\mu\text{g/L}$ Hg by amalgamation
(1 mL sample)	0.030

The influence of the reaction coil size and oxidation state on the peak height sensitivity (sample: 10  $\mu\text{g/L}$  As)

Coil length [cm]	Coil I.D. [mm]	As <sup>3+</sup>	As <sup>5+</sup>
7	0.5	0.491	0.014
67	1.0	0.640	0.040
210	1.3	0.790	0.185

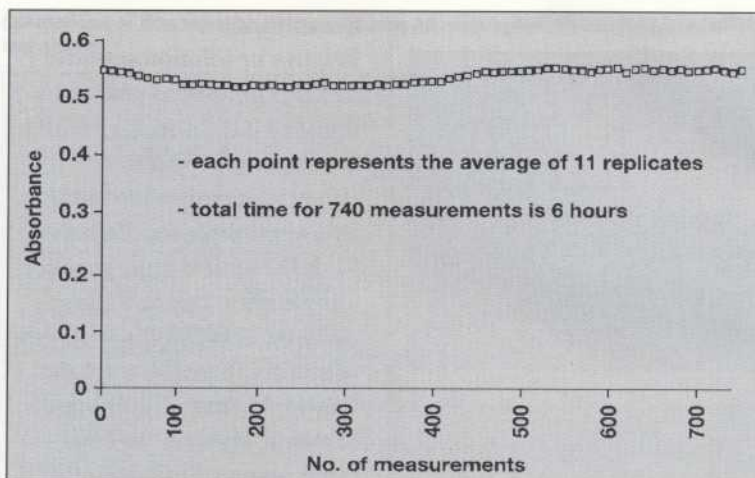
The amount of time allowed for the reaction of the reductant and sample may also affect the sensitivity. The reaction time is determined by the length of the reaction and stripping coils. The reaction coil joins the reductant and sample inlets to the argon inlet in the mixing unit. The stripping coil joins the mixing unit and the gas liquid separator. The use of a longer reaction coil results in increased reaction times.

Since with FI-MH relatively small sample volumes are used reaction times are very short. Compared to batch techniques sensitivity of FI-MH is much less affected by interfering elements.

## Precision

The precision of a FI-MH analysis depends 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 leaks, and by proper programming of the flow injection system. Suspended solids should be removed from all solutions to ensure consistent and unimpeded flow of the sample and reagents.

The system software for the Perkin-Elmer FIAS controls the sequence of the determination using three basic steps. The first, a prefill step is for filling the tubing from the auto-sampler 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. All Perkin-Elmer instruments with FIAS control capabilities have stored default programs to facilitate the programming of the Flow Injection System.



FI-MH Long-term Performance Demonstrated with the Determination of 10 µg/L Arsenic

## Unmached Detection Limits

The analytical performance of FI-MH is exceptional as shown by the detection limits in the following table.

Equally impressive is the performance of the FI mercury/hydride technique for the analysis of samples with complex matrices. As the element to be determined is separated from the sample matrix, measurement takes place practically free of matrix interference and non-specific absorption.

Detection limits with the FI-MH-AA technique for aqueous solutions (500 µL)

	Absolute (ng)	Relative (µg/L)
As	0.025	0.050
Bi	0.020	0.040
Sb	0.023	0.045
Se	0.020	0.040
Sn	0.050	0.100
Te	0.055	0.110
Hg*	0.006	0.006

\* Hg detection limit using amalgam technique



# FI-MH – Wide Range of Applications

The range of applications of FI-MH is wide-spread. The following table gives an over-

view of applications done to date in our laboratory.

Matrix	Element
Body fluids	As, Se, Hg
Sewage sludge, waste water	As, Hg
Sediments	As, Hg
Drinking water, mineral water	As, Hg
Samples of biological origin:	
Bovine liver, animal muscle,	
Wheat and rice flours	Se
Fly ash	As, Se, Sb
Steels	As, Bi, Sb, Se
Spinach, orchards leaves,	
Pine needles	Hg
AgNO <sub>3</sub>	

## Determination of Selenium in Biological Materials

	Selenium content [ $\mu\text{g/g}$ ]	
	Measured	Certified
Oyster Tissue (NBS 1566)	$2.07 \pm 0.05$	$2.1 \pm 0.5$
Wheat Flour (NBS 1567)	$0.97 \pm 0.03$	$1.1 \pm 0.2$
Rice Flour (NBS 1568)	$0.34 \pm 0.01$	$0.4 \pm 0.1$
Bovine Liver (NBS 1577)	$1.10 \pm 0.03$	$1.1 \pm 0.1$
Animal Muscle (IAEA H-4)	$0.34 \pm 0.01$	0.28

## Determination of As in Tap and Mineral Waters

Very common examples for the determination of As with FI-MH can be found in the field of water analysis. This example shows the determination of tap water and three different mineral waters by FI-MH.

Samples were prepared as follows: If necessary, samples should be degassed in an ultrasonic bath. A mixture of 10 mL of sample, 3 mL conc. HCl, and 1 mL KI solution (5% KI + 5% ascorbic acid) was allowed to stand for one hour at room temperature.

Results	As ( $\mu\text{g/L}$ )	% RSD
Tap water	1.45	0.7
Mineral water #1	14.5	0.6
Mineral water #2	15.7	1.7
Mineral water #3	0.44	2.9

## Determination of As in Waste Water

The following table shows a comparison of characteristic data for FI-MH and batch systems for a determination of As in waste water.

	FI-MH-AA	Batch System
Sample (mL)	0.5	5
Concentrated Hydrochlorid acid (mL)	0.5	5
Potassium iodide (mg)	3	30
Ascorbic acid (mg)	5	50
Borohydride (mg)	15	150
Samples per hour	120 - 180	3

### Determination of As in Urine

The following describes a procedure for the determination of arsenic in urine that significantly reduces method time and complexity. The combination of the hydride technique and flow injection results in significant savings in time and a miniaturization of the reaction chamber to reduce matrix influences and chemical consumption.

The procedure describes the determination of arsenic in urine without the need for a sample digestion. This prevents the determination of irrelevant arsenic compounds that, per example occur when fish is consumed prior to sampling. The increased sensitivity of the flow injection technique permits the dilution of the urine sample, thereby reducing the matrix influence.

The procedure was tested in a collaborative study by the German Society of Occupational Medicine.

### Determination of As, Bi, Sb, and Se in Steel

In contrast to batch-type hydride systems, FI-MH requires only a single set of

### Sample Preparation

The urine sample was diluted 1:20 with distilled water. To reduce the  $\text{As}^{5+}$  to  $\text{As}^{3+}$ , 5 mL of the diluted urine was placed in an autosampler tube and 3 mL of 32% HCl and 1 mL of a 10% KI solution was added. The mixture was shaken well and allowed to reduce for 1 hour at room temperature. A dilution series of aqueous arsenic solutions within the concentration range 2  $\mu\text{g/L}$  to 20  $\mu\text{g/L}$  was prepared for parallel determination. On completion of the reduction time, all the solutions were measured.

The following table shows the time required for this procedure in comparison with alternative AAS techniques. Duplicate determinations of 20 samples, including any necessary calibration steps, were used as a basis for establishing the time required. All times are given as hours:minutes.

It is important to point out that when using the graphite furnace AAS technique the total concentration of arsenic is determined, including any toxicologically irrelevant compounds that may also be present.

	Graphite Furnace [h:min]	MH-Batch System [h:min]	FI-MH-AAS [h:min]
Sample preparation	0:10	0:15	0:15
Solution preparation	0:20	1:30	1:00
Measurement	3:10	2:25	0:40
Total*	3:40	4:10	1:55
*includes real working time of:	0:30	4:10	1:15

recommended analytical conditions for the determination of all the hydride-forming elements in steel samples. Approximately 0.5 g of steel

were accurately weighed and transferred to a graduated cylinder. Aqua regia (12 mL) was added and the sample was heated at 90°C.

	Sb [ $\mu\text{g/g}$ ]		As [ $\mu\text{g/g}$ ]		Bi [ $\mu\text{g/g}$ ]		Se [ $\mu\text{g/g}$ ]	
Sample	Measured	Certified	Measured	Certified	Measured	Certified	Measured	Certified
NBS-361	46 $\pm$ 3	42 $\pm$ 5	180 $\pm$ 2	170 $\pm$ 10	5 $\pm$ 0.5	(4)	34 $\pm$ 3	40 $\pm$ 10
NBS-362	120 $\pm$ 4	130 $\pm$ 10	820 $\pm$ 10	920 $\pm$ 50	26 $\pm$ 0.5	(20)	11 $\pm$ 0.5	12
NBS-363	15 $\pm$ 2	20 $\pm$ 10	90 $\pm$ 1	100 $\pm$ 10	6 $\pm$ 6	(8)	1.8 $\pm$ 0.1	(1.6)
NBS-364	320 $\pm$ 10	340 $\pm$ 10	400 $\pm$ 20	520 $\pm$ 50	14 $\pm$ 0.5	(9)	1.8 $\pm$ 0.1	(2.1)



# Fully Automated Hg Determination (FIMS)

## **FIMS - A fully automated, fast and cost-effective trace mercury analyzer**

The Perkin-Elmer Flow Injection Mercury System (FIMS) is a small, easy-to-operate atomic absorption system dedicated to trace mercury analysis. Based on flow injection techniques, it is fully automated, fast and cost-effective. The FIMS is a stand-alone system consisting of a high sensitivity spectrometer with a high energy mercury source, precision long-path absorption cell and solar-blind detector; and a built-in flow injection system. Mercury detection limits of  $<0.01 \mu\text{g/L}$  (relative) or  $0.005 \text{ ng}$  (absolute) are obtained routinely with FIMS. These levels are well under the current maximum allowable limits for mercury in drinking water set by regulatory agencies. Equally impressive is the performance of FIMS for the analysis of samples with complex matrices. Use of the flow injection technique reduces matrix effects and, because the Hg is released from the matrix, measurements are virtually free of non-specific absorption. In addition, memory effects are much lower compared to continuous flow mercury analyzers, even with large variations in Hg concentration.

FIMS provides maximum sample throughput of up to 2 determinations per minute. In addition, the optional AS-91 autosampler can hold up to 218 samples and analyze them in

Mercury concentration ( $\mu\text{g/L}$ ) of several control samples

	Result measured	Value given
Lanonorm metals 1	$11.4 \pm 0.2$	$11.8 \pm 2.0$
Lanonorm metals 2	$119 \pm 3.0$	$114.0 \pm 13$
Lyphocheck urine 1	$7.8 \pm 0.9$	$5.2 \pm 2.4$
Lyphocheck urine 2	$31.3 \pm 1.9$	$30.5 \pm 10$
Seronorm urine 115	$33 \pm 0.5$	35

any desired sequence. The software monitors and controls the entire process, including periodic recalibrations and check sample analyses performed according to protocols set by regulatory groups, such as the US Environmental Protection Agency (EPA). FIMS reduces operating costs. Reagent and carrier gas consumption are much lower with FIMS than with conventional continuous flow systems. FIMS offers the choice of using  $\text{SnCl}_2$  (according to EPA protocols) or  $\text{NaBH}_4$  reducing agents. With its peristaltic pumps, FIMS can also automatically add additional reagents such as  $\text{KMnO}_4$  for stabilization of the mercury.

FIMS is a small instrument requiring minimal bench space.

## **Determination of Mercury in Urine**

The determination of mercury in various biological matrices, particularly in blood and urine, is becoming more and more important in the assessment of mercury contamination in the environment, in general, and in the work place in particular.

To determine the total concentration of mercury in urine samples, it is necessary to use a technique which destroys any organic mercury compounds present and converts them into ionic mercury. The method here uses the automatic on-line addition of potassium permanganate and an oxidation agent, enabling the total concentration of mercury in urine to be determined directly.

It is possible to determine the total concentration of mercury in urine samples with very little sample preparation. Using the flow injection technique, the analytical process is automated. The method provides a low detection limit and a wide dynamic range, thus fulfilling all of the requirements for routine use in clinical chemistry.



# Automatic Amalgamation

## Determination of Mercury in an Excess of Silver Nitrate

Silver nitrate is an essential raw material for the production of light-sensitive materials in the photo and film industry. Since mercury, even at very low concentrations, will interfere with the manufacturing process, it is necessary to constantly monitor the silver nitrate for mercury.

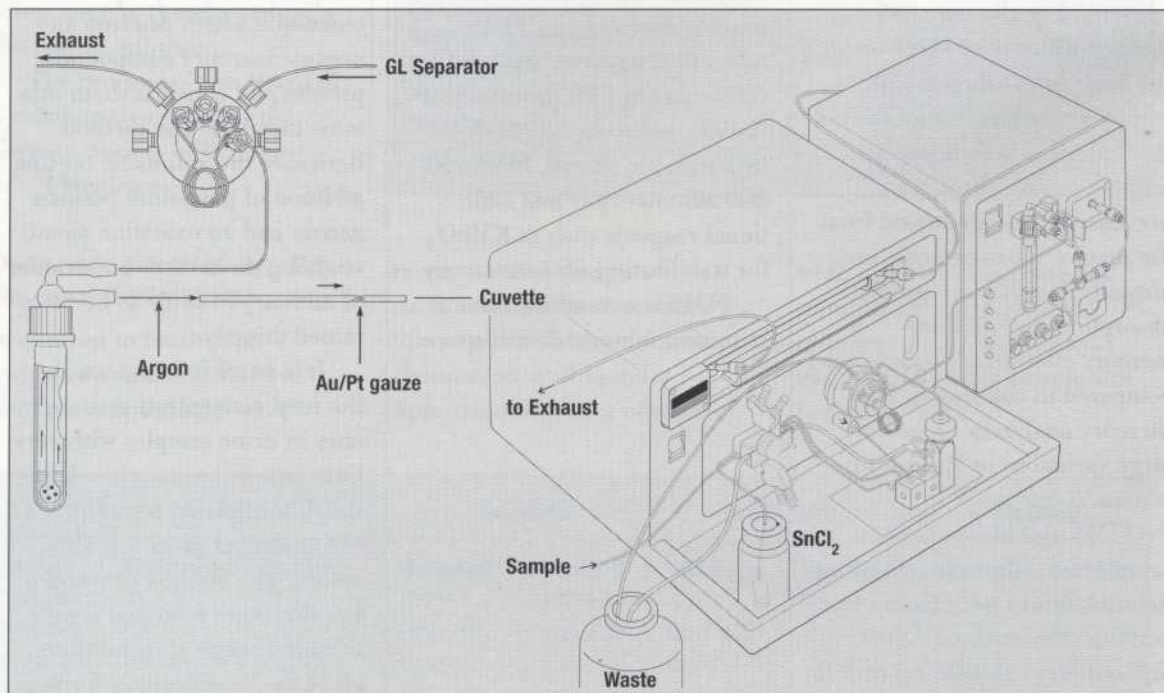
However the determination of low levels of mercury in the presence of high concentrations of silver or silver nitrate is very tedious. The most sensitive procedure for the determination of mercury is the cold vapor technique. The use of flow injection to

automatically generate the cold vapor mercury increases sample throughput and results in a reduction of interferences from the presence of silver nitrate.

Optimum results can be obtained using low concentrations of  $\text{NaBH}_4$ , which minimizes the reduction of the silver nitrate. Higher acid concentrations reduced the memory effects and interferences associated with this analysis. Thus, when using both thiourea and  $\text{HNO}_3$  in the carrier solution, mercury can be determined accurately in the presence of up to 5 g/L  $\text{AgNO}_3$  or, with smaller injected volumes, up to 20 g/L  $\text{AgNO}_3$ . The detection limit ( $3\sigma$ ) of mercury in the presence of 2  $\mu\text{g/L}$   $\text{AgNO}_3$  is 0.25  $\mu\text{g/L}$ .

## Computer-controlled Automatic Amalgamation

The sensitivity for mercury can be significantly improved using the FIAS with its automatic amalgamation attachment. In essence, the amalgamation system is an on-line analyte concentration technique which can improve the detection limit for mercury by an order of magnitude or more when increased sample volumes are used. The detection limits obtained are well under the current maximum allowable limits for mercury in drinking water set by regulatory agencies such as the U.S. Environmental Protection Agency.



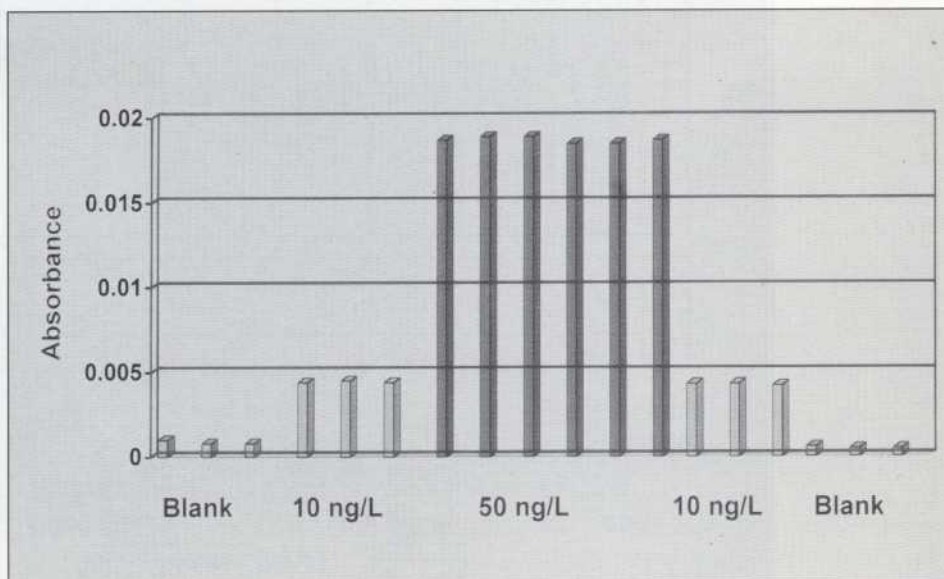
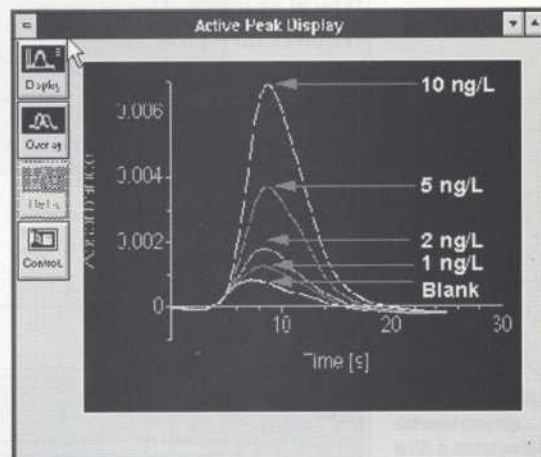
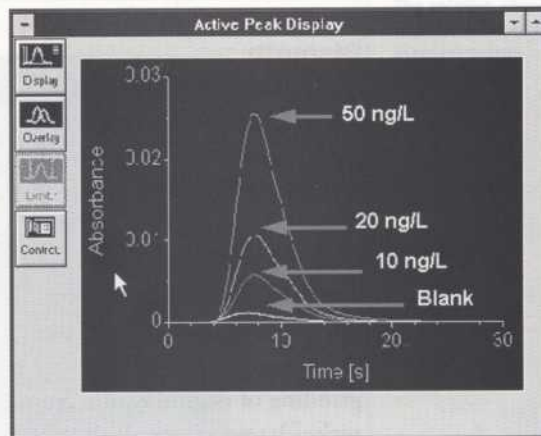
### Automatic amalgamation provides:

- Increased sensitivity for mercury and improved detection limits of more than one order of magnitude.
- Fully automated operation in connection with the FIAS Flow Injection System.
- Automatic change-over from amalgamation to non-amalgamation or hydride operation or vice versa in a sequential multielement run.
- Simple operation via instrument control software, with all parameters under computer control.

Using the amalgamation attachment the mercury vapor generated in the FIAS is first passed through the amalgamation system before it reaches the quartz cell in the sample beam of the AA spectrometer. In the amalgamation system the mercury vapor is freed from residual reaction products in a wash bottle, dried in a drying tube, and then carried into the amalgamation tube. The amalgamation tube is a quartz tube filled with a fine gold-platinum gauze. The mercury is preconcentrated on the Au/Pt-gauze by amalgamation. The total amount of Hg collected on the Au/Pt-gauze depends on the collection time when working in continuous mode, or on the volume injected when working in the FI mode.

At the end of the collection time the amalgamation tube is rapidly heated to approximately 600 °C. The total amount of mercury collected on the Au/Pt-gauze is rapidly desorbed and transported to the absorption cell.

Hg determination in the ng/L range using the FIMS



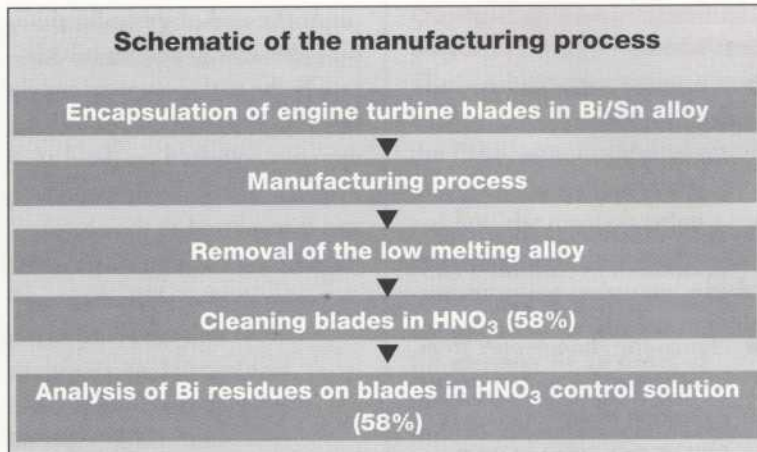
Precision of Hg determination in the ng/L range using the FIMS with amalgamation



# FI-MH Automatic Process Control

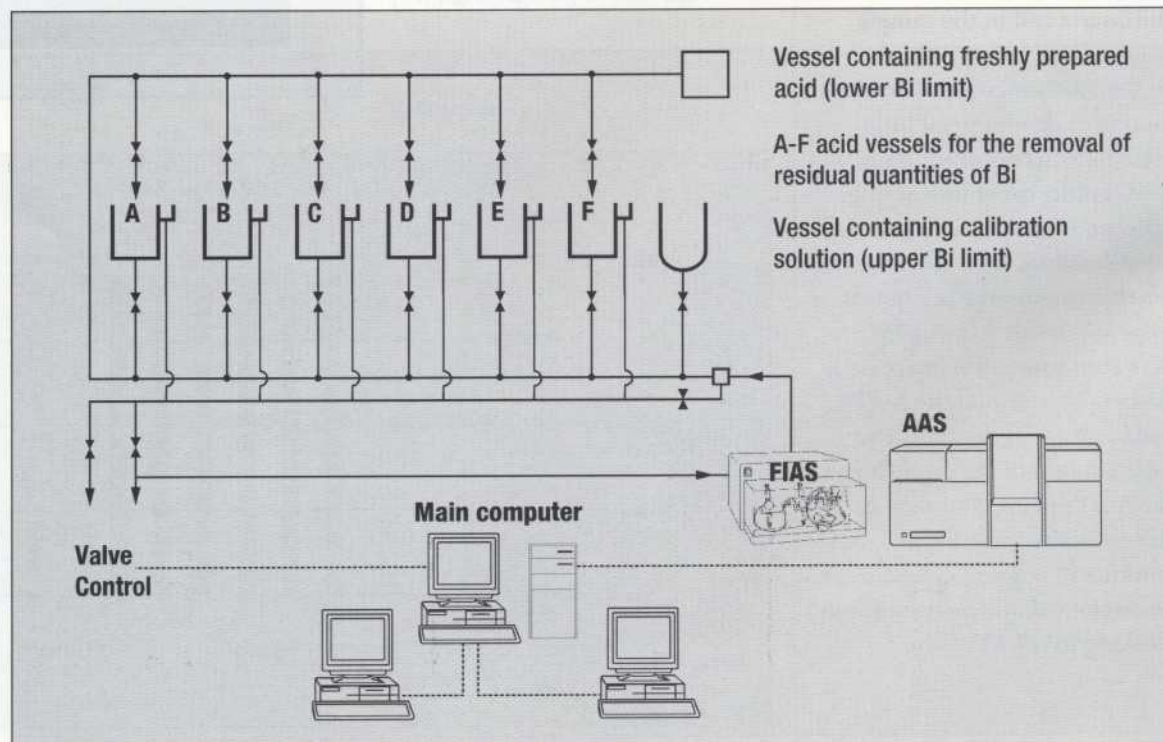
## On-line Determination of Bismuth

In the manufacture of components for aircraft engines, many control procedures are necessary to guarantee the desired product quality. To limit the substantial costs involved, many of these production and control processes are being automated. The grinding of engine blades from nickel-based material is a typical example. This process requires the blades to be encapsulated using a low melting Bi/Sn alloy. On completion of the grinding process, the alloy is melted out and the residual amounts are removed



with 58% nitric acid solution. The Bi/Sn must be removed from the blades since Bi attacks the blade material at the high operating temperatures of the engine. To establish the Bi

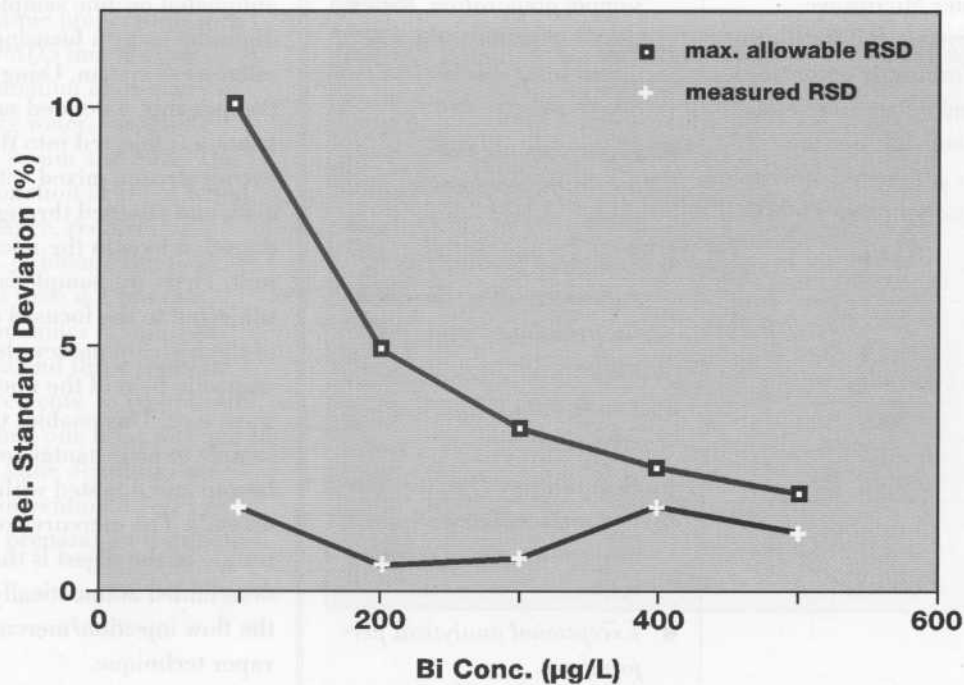
residue subsequent to the cleaning process, the blades are first treated with a test solution of HNO<sub>3</sub>. The cleaning process is automated and controlled by automated on-line monitoring of the Bi content using FI-MH.



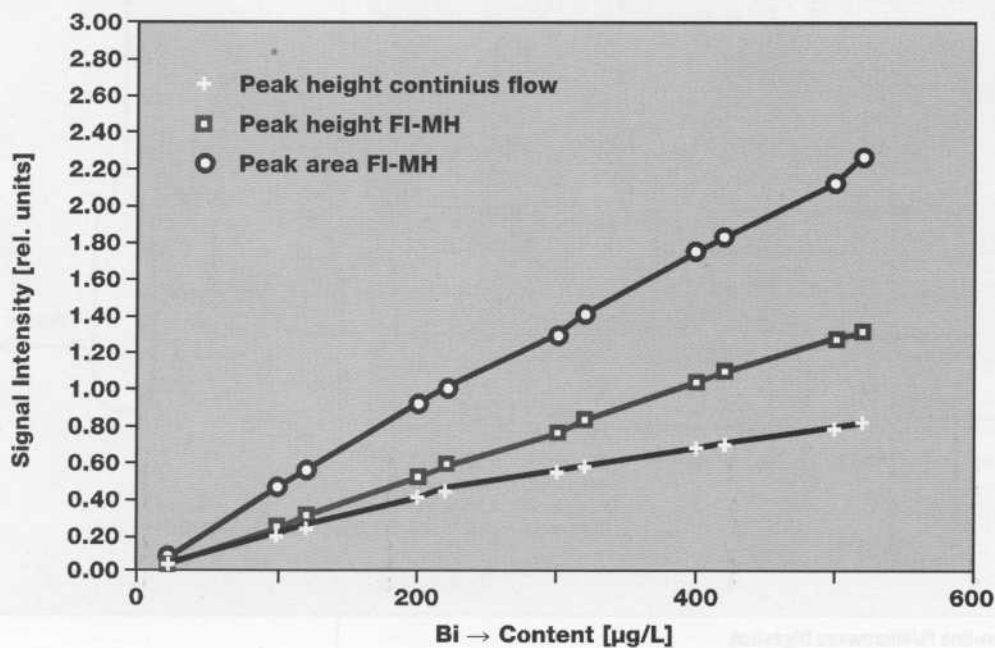
Schematic of integrated process



# (2014) *Journal of Environmental Monitoring* Digestion and Determination of Bi in Water, Blood, Urine and Milk with FI/MDS



The relative standard deviation of Bi measurements with a FI-MH



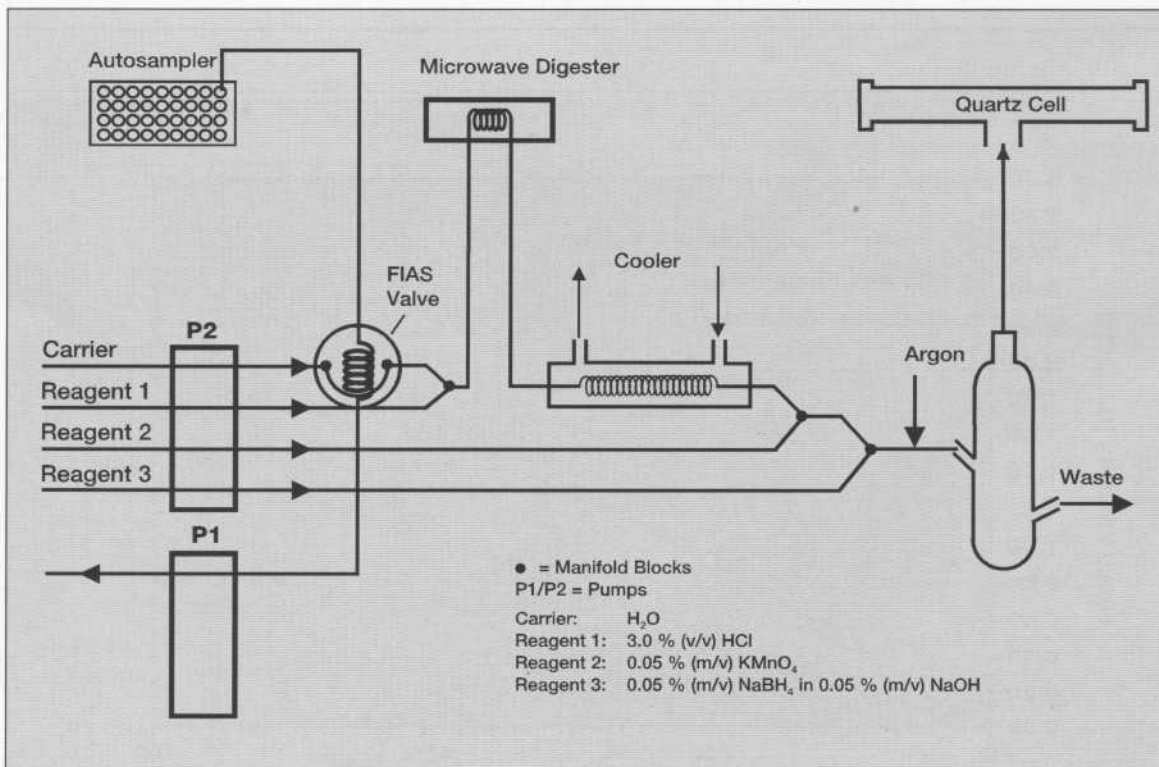
Comparison of sensitivity for Bi measurements with a commercial continius flow system and FI-MH

# On-line Microwave Digestion (FI/MDS)

Combining FI-MH with the Perkin-Elmer Microwave Digestion System (MDS) allows you to perform fully automated on-line sample digestion. Some of the key benefits you can obtain with automated on-line sample digestion using FI-MH include:

- Significant time savings for sample preparation. For example, digestion of a 500  $\mu\text{L}$  serum sample takes less than 30 seconds.
- Higher sample throughput due to shorter total analysis times.
- Enhanced productivity by fully automating the analysis, including sample preparation.
- Lower sample and reagent consumption.
- Reduced risk of contamination and analyte loss through the use of a closed system.
- Exceptional analytical performance.

FI-MH is ideally suited for automated on-line sample digestion using a focusing microwave system. Using the FI components, a defined sample volume is injected into the carrier stream, mixed with the acid, and pumped through the digestion loop in the microwave unit. There the sample is subjected to the focused energy of the high-frequency electromagnetic field of the microwave unit. This enables the sample to be instantaneously heated and digested within seconds. The mercury concentration in the digest is then determined automatically by the flow injection/mercury cold vapor technique.



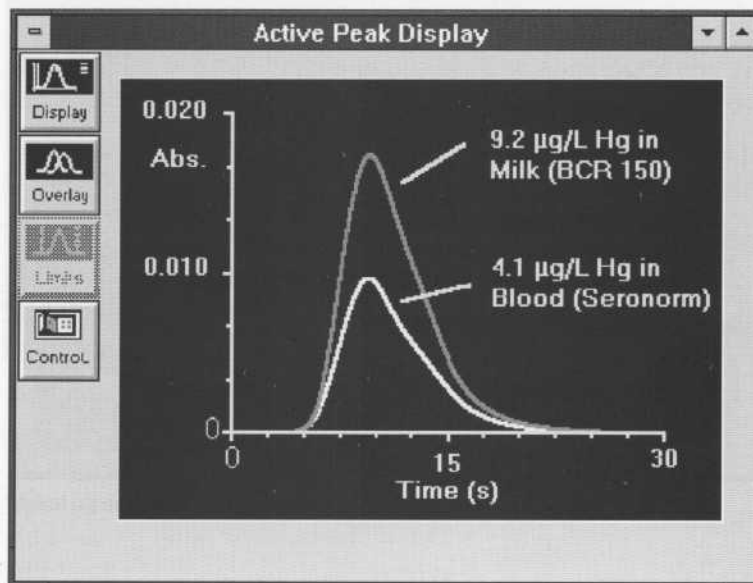
Schematic of on-line FI/Microwave Digestion

# Digestion and Determination of Hg in Water, Blood, Urine and Milk with FI/MDS

Examples of automated on-line sample preparation with the FI/MDS include the determination of mercury in drinking water, wastewater, blood, serum and milk. The determination of Hg in blood, for instance, requires only 500  $\mu\text{L}$  of blood. The total analysis time is 4 minutes, which includes sample preparation and three replicate measurements. In comparison, more than one hour is required for the same determination using conventional "off-line" sample preparation techniques.

Analysis control via measurement of control samples after on-line microwave digestion

Sample	Measurement value ( $\mu\text{g/L}$ )	Nominal value ( $\mu\text{g/L}$ )
<b>Urine:</b>		
Lyphocheck 1	$7.8 \pm 0.9$	$5.2 \pm 2.4$
Lyphocheck 2	$31.3 \pm 1.9$	$30.5 \pm 10$
<b>Blood:</b>		
Seronorm 010010	$4.1 \pm 0.6$	$4.2 \pm 0.9$
Seronorm 906	$15.0 \pm 0.8$	$15.0 \pm 1.1$
<b>Milk:</b>		
BCR No. 150	$9.2 \pm 2.0$	$9.4 \pm 1.7$
BCR No. 151	$91.3 \pm 4.4$	$101.0 \pm 10$
<b>Saliva:</b>		
1120/1	6	5.5
1120/2	29.2	30.9
<b>Waste:</b>		
1395/3	$116 \pm 4$	120
1795/4	$2.2 \pm 0.02$	2.1



Determination of Hg in milk and blood after on-line microwave digestion



**Determination of Hg in Biological Samples with the FIMS 400 after On-line Microwave Digestion**

	Water	Urine	Blood	Milk	Saliva
<b>Detection Limit (µg/L)</b>	0.03	0.05	0.1	0.1	0.1
<b>Working Range (µg/L)</b>	0.3 - 100	0.5 - 150	1.0 - 300	1.0 - 300	1.0 - 300
<b>Sample Consumption (mL)</b>	5	5	0.5	0.5	0.5
<b>Time per Determination n = 3 (min)</b>	4	2	4	4	4
<b>Microwave Power (Watt)</b>	60	—	60	60	—

**FIAS On-line Microwave Digestion  
Total Hg in Blood - Method Comparison**

	FI On-line Digestion	Pressure Digest with FI	Batch System Direct with Amalgam
<b>Detection limit, µg/L in blood</b>	0.1	0.1	1
<b>Working range, µg/L in blood</b>	1-300	1-300	5-50
<b>Time/sample</b>	4 min.	>1hour	10 min.
<b>Sample consumption (n = 3)</b>	0.5mL	1.0mL	1.5mL

# Digestion and Determination of Hg in Blood with FI/MDS

The determination of mercury in blood is used to monitor mercury contamination in the workplace and in the environment.

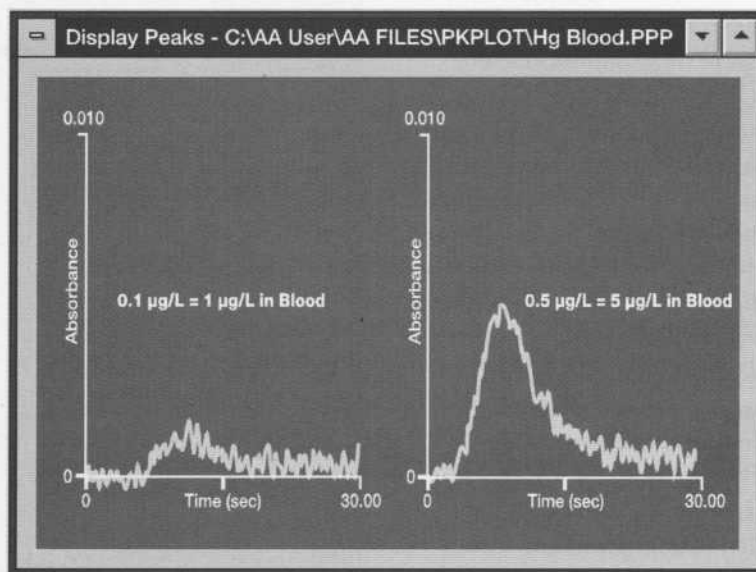
To accurately determine the total mercury in blood, it is first necessary to digest the samples to convert any organic mercury compounds to ionic mercury. In the automatic method described here, an oxidation reagent and microwave radiation are used to digest the samples prior to the mercury determination using flow injection techniques.

A Perkin-Elmer FIAS flow injection system and AS-90 autosampler were used for flow injection sample preparation and sampling. A Prolabo Maxidigest MX-350 was used for on-line digestion of the blood samples. The MX-350 was controlled by the FIAS system using a special interface. Detection was performed with a Perkin-Elmer Model 4100 AA spectrometer. To obtain an optimum signal-to-noise ratio, a System 2 electrodeless discharge lamp (EDL) power supply and Hg EDL were used. The determination was also performed with a Perkin-Elmer FIMS 400 instrument.

The system tubing configuration and the various system components (microwave, cooling system, reagents, etc.) are shown in the figure on page 36.

Comparison with an off-line digestion procedure and with a direct procedure using amalgamation confirmed the need to digest the blood samples in order to obtain accurate results. The comparison showed that on-line digestion was superior to the off-line method with regard to sample throughput, sample consumption, and total measurement time.

The accuracy of the procedure was tested with control samples. The table below lists the results obtained. The figure at the bottom shows a signal measured near the detection limit, and another signal in the range of 5  $\mu\text{g/L}$  Hg in blood. The linear range extends to approximately 300  $\mu\text{g/L}$  in blood. The detection limit is 1  $\mu\text{g/L}$  Hg in blood with a sample volume of 500 mL and dilution of the original sample by a factor of 10. Sample throughput is approximately 45 measurements per hour.



Typical signals for the determination of Hg in blood.

Determination of Hg ( $\mu\text{g/L}$ ) in blood control sample

Control sample	Measured value	Nominal value
Seronorm No. 010010	$4.1 \pm 0.6$	$4.2 \pm 0.9$
Seronorm No. 905	$9.5 \pm 0.8$	$10.0 \pm 0.5$
Seronorm No. 906	$15 \pm 0.8$	$15 \pm 1.1$
Behring No. 62 0401	$103 \pm 2.0$	$90.2 \pm 8.3$

# Determination of Total Hg in Environmental Samples with FI/MDS

## Determination of Total Hg in Environmental Samples with On-Line Microwave Digestion

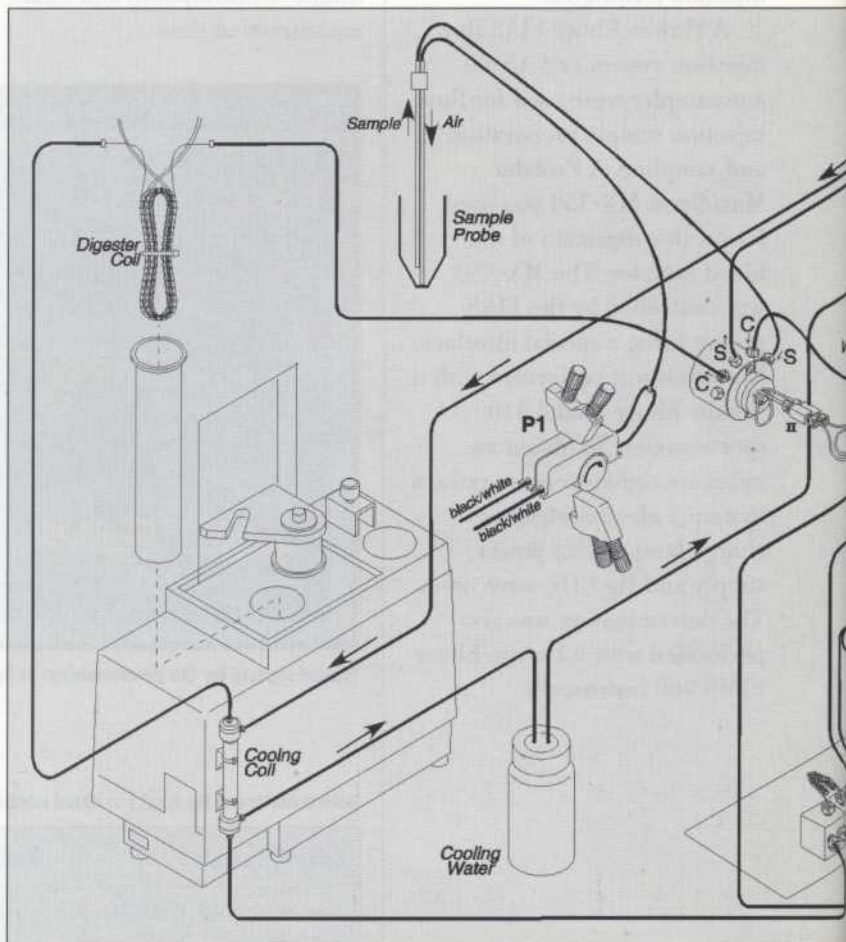
The FIMS coupled with an on-line microwave digestion system fully automates the digestion and determination of total mercury in environmental samples (drinking waters, wastewaters and sediments). Once appropriate digestion reagents are added to the sample, the entire system operation occurs automatically. The time required for sample digestion has been reduced from 0.5-2 hours to less than 1 minute. Three replicate determinations of a single sample can be performed in 5 minutes. The system demonstrates exceptional accuracy for drinking water and wastewater samples spiked with inorganic mercury and methylmercury chloride; wastewater samples digested off-line and analyzed with conventional flow injection-mercury cold vapor AAS; and spiked and unspiked certified sediment samples. The precision for a 10 ng/mL Hg standard is comparable to that obtained without on-line microwave digestion (1.1% RSD,  $n=3$ ). The detection limits for the on-line microwave digestion-FIMS combination are also quite low due to the exceptional stability of the

FIMS, with an instrument detection limit (IDL) of 0.014 ng/mL Hg and a method detection limit (MDL) of 0.035 ng/L Hg for a 500 mL sample volume. Since the entire

analytical process occurs in a closed system, opportunities for contamination are greatly reduced, leading to greater analytical quality and enhanced laboratory productivity.

Analytical results for sediment slurries analyzed with on-line microwave digestion with FIMS detection. "BCSS-1" is a marine sediment from the Canadian National Research Council, and "SRM 2704" is a river sediment (Buffalo River sediment) from the National Institute For Standards and Technology. The concentrations are back-calculated to the original sediment sample and to standard deviation ( $n=3$ ).

Sample	Certified (mg/g)	Found (mg/g)
BCSS-1	$0.129 \pm 0.012$	$0.20 \pm 0.1$
BCSS-1 + 4.0 $\mu\text{g/g}$ Spike	$4.129 \pm 0.012$	$4.27 \pm 0.4$
SRM 2704	$1.47 \pm 0.07$	$1.54 \pm 0.$



On-line microwave digestion manifold with automated sample agitation for determining total Hg in environmental samples.



# Literature for FI-MH AA

## Flow Injection Application Summary

### Literature for FI-Mercury/Hydride AAS

Analyte		Perkin-Elmer Literature No.
As	Urine	TSAA-23E
As	Sediments	TSAA-12E
As	Drinking Water	TSAA-12E
As, Bi, Sb, Se	Steel	TSAA-12E
As, Se, Sb	Fly Ash	TSAA-12E
Hg	Urine	TSAA-26E
Se	Biol. samples	TSAA-12E
Sn	Steel	TSAA-49E
Hg	Blood, on-line Digestion	TSAA-35E
Sn	Steel	AS-1218
As, Bi, Hg, Sb	Geol. samples	AS-1219
Hg	On-line Digestion	AS-1220
Theory	Optimization of Parameters	AS-1193
Hg	Blood	AS-1192
As (species)	Urin, Seafood	AS-1184
Hg	Drinking Water	ENV-12A
Hg	Environmental samples	AS-1186
Hg	Water, Urine	AS-1181
Hg	Air	AS-1030
Hg	Drinking Water	TSAA-36
Hg	TCLP Extracts	TSAA-28
Theory	Affecting Factors	TSAA-17
Theory	Optimization of Parameters	AS-1162

