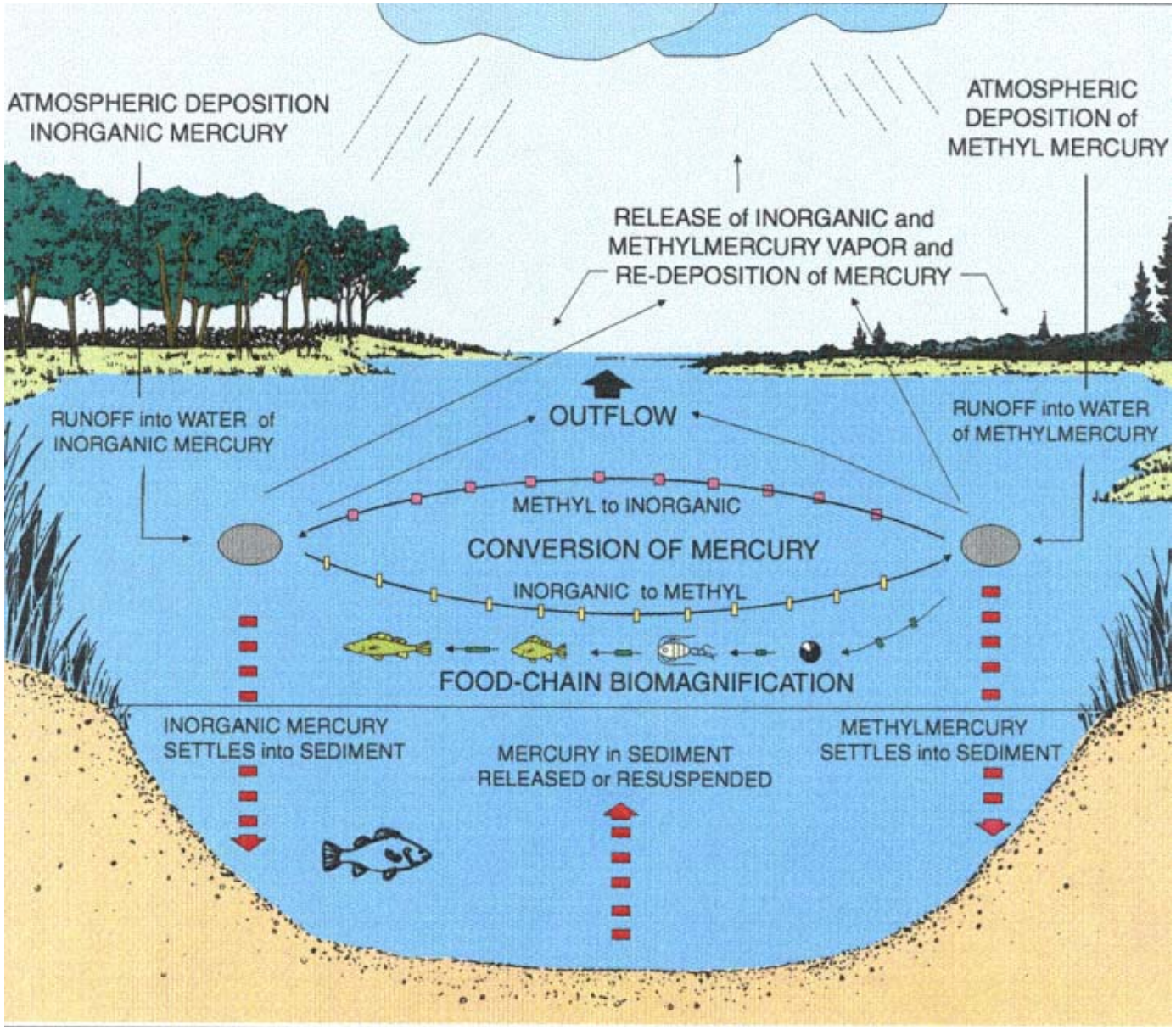
DMA-80
Direct Mercury Analyzer

Milestone Srl

Introduction

- Mercury in the atmosphere can be from manmade sources (coal-fired power plants, municipal incinerators, industrial boilers) or from natural sources (forest fires, geologic formations, volcanoes)
- Precipitation is the primary mechanism for transporting airborne gaseous or particulate mercury from the atmosphere to surface water and land


ATMOSPHERIC DEPOSITION
INORGANIC MERCURY
ATMOSPHERIC
DEPOSITION of
METHYL MERCURY
RELEASE of INORGANIC and
METHYLMERCURY VAPOR and
RE-DEPOSITION of MERCURY
RUNOFF into WATER of
INORGANIC MERCURY
OUTFLOW
RUNOFF into WATER
of METHYLMERCURY
METHYL to INORGANIC
CONVERSION OF MERCURY
INORGANIC to METHYL
FOOD-CHAIN BIOMAGNIFICATION
INORGANIC MERCURY
SETTLES into SEDIMENT
MERCURY in SEDIMENT
RELEASED or RESUSPENDED
METHYLMERCURY
SETTLES into SEDIMENT

Mercury Analysis

Method	Technique	Sample type
7470A	CV-AAS	Liquid waste
7471A	CV-AAS	Solid or semi-solid waste
7472	ASV	Aqueous samples and extracts

CV-AAS

- Cold Vapor-Atomic Absorption Spectroscopy
  - Samples are digested or dissolved
  - Mercury is reduced to free atomic state by using tin (II) chloride or sodium boro-hydride in a closed reaction vessel
  - Mercury is measured by atomic absorption

CV-AAS

Step	Description	Time
Sample acid digestion	Hot plate	2 hours- 2 days
	Closed vessel microwave	20 minutes- 1 hour
Wet chemistry	Interference removal	1 hour
	Mercury reduction	
Analysis	AAS	Few minutes

CV-AAS and ASV

- Both methods require sample digestion and further wet chemistry
- Sample digestion can be problematic because of Hg volatility
- Sample preparation is the bottleneck for higher analytical productivity

DMA-80
Direct Mercury Analyzer

DMA-80 Advantages

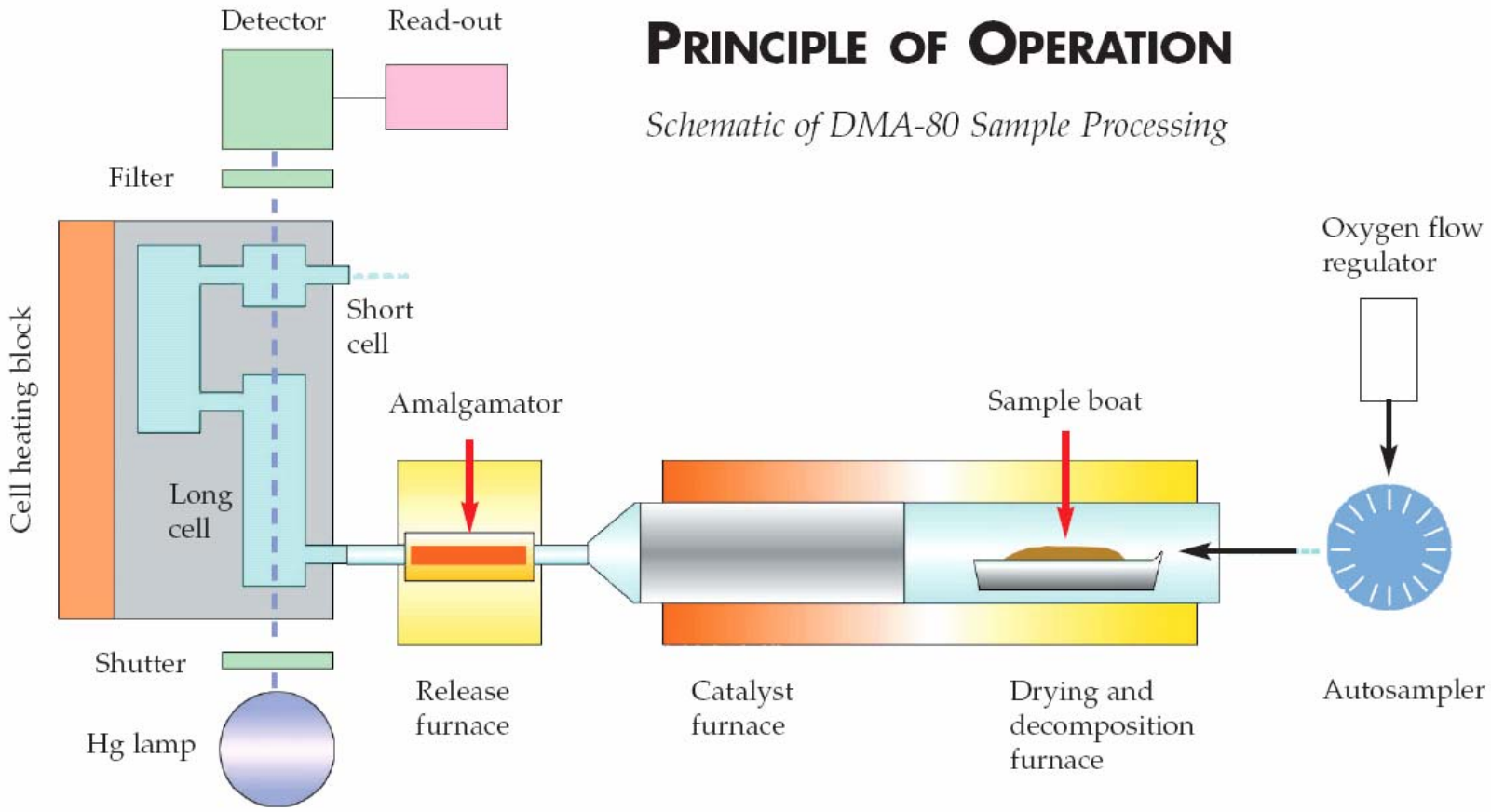
- Direct Hg determination at trace level on solid and liquid samples
- No sample digestion step
- No wet chemistry pre-treatment step
- Fast, approximately 6 minutes per sample
- Eliminates waste disposal
- Validated results (US EPA method 7473) for solid and liquid matrices

DMA-80
Principle of operation

- Solid or liquid samples are weighed and introduced in the DMA-80
- The sample is initially dried and then thermally decomposed in a oxygen flow
- Combustion products are carried off and further decomposed in a hot catalyst bed
- Mercury vapors are trapped on a gold amalgamator and subsequently desorbed for quantitation
- The mercury content is determined using atomic absorption spectrophotometry at 254 nm

PRINCIPLE OF OPERATION

Schematic of DMA-80 Sample Processing



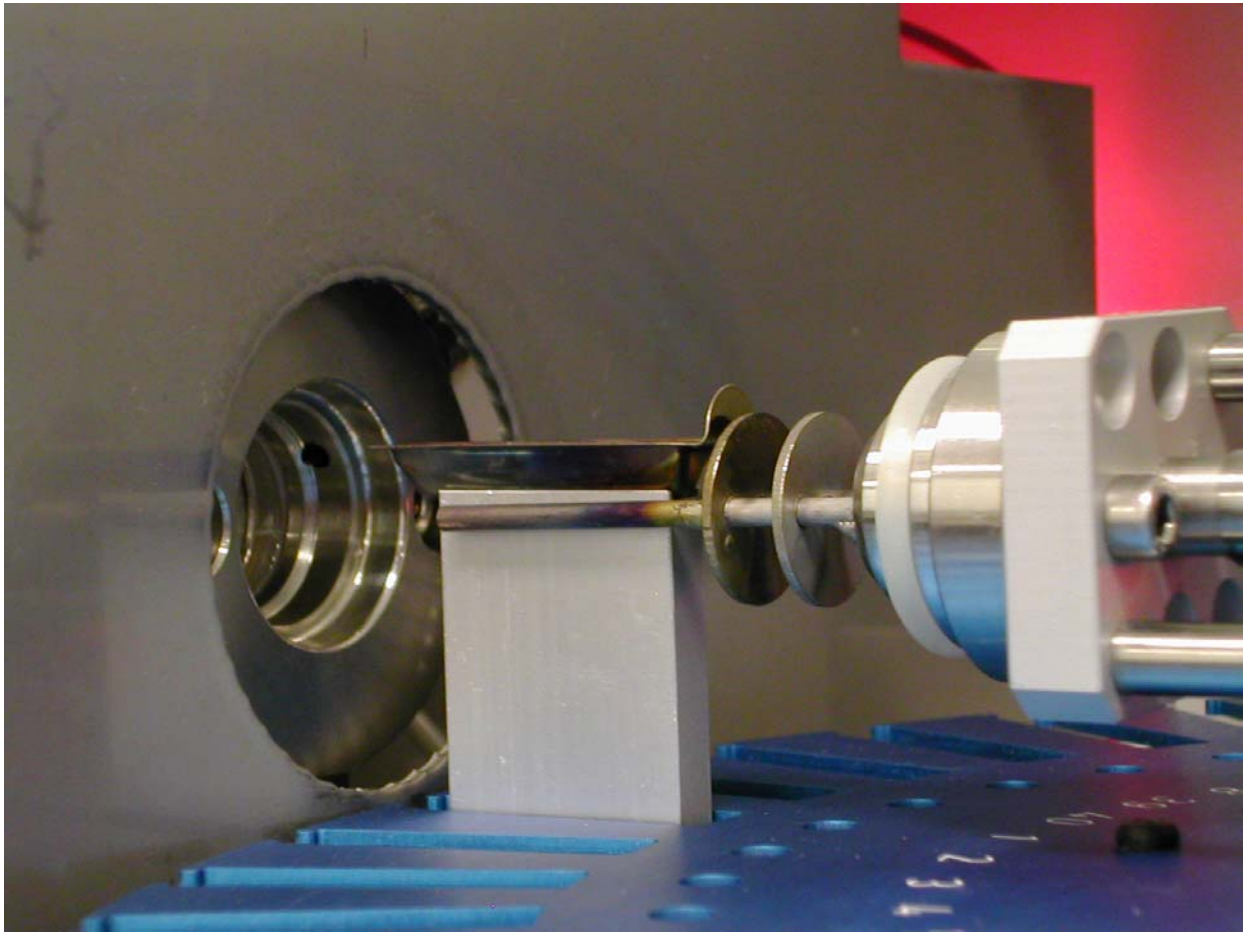
DMA-80

- Major components
  - Sample dosing system
  - Thermal process furnaces
  - Atomic absorption spectrophotometer
  - System controller

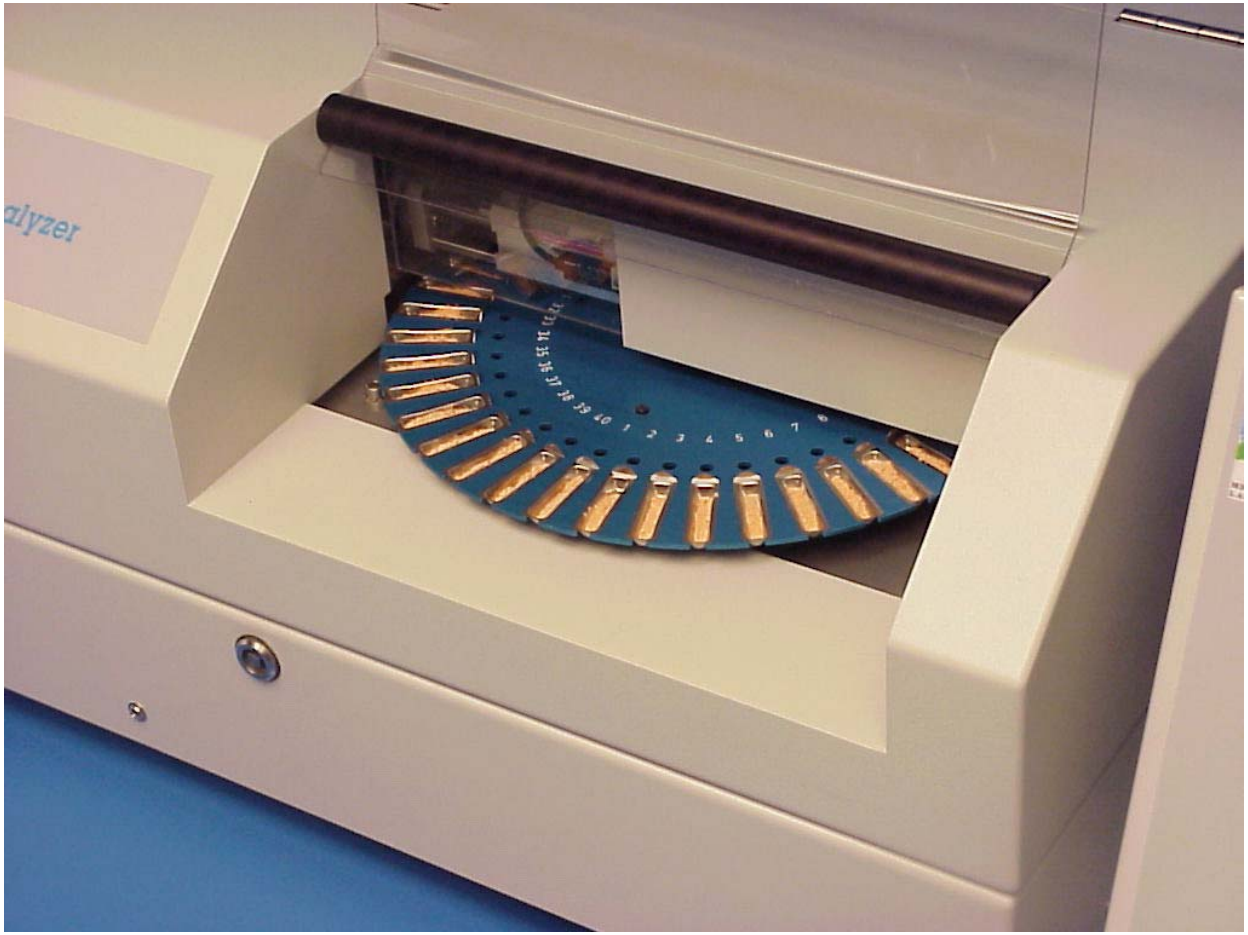
Sample Dosing System

- Built-in 40 position auto-sampler for high throughput unattended operation, for solid and liquid samples
- Maximum sample weight 500 mg
- Maximum sample volume 500 µl
- Possibility of multiple sample dosing for Hg pre-concentration on amalgamator

Sample Introduction

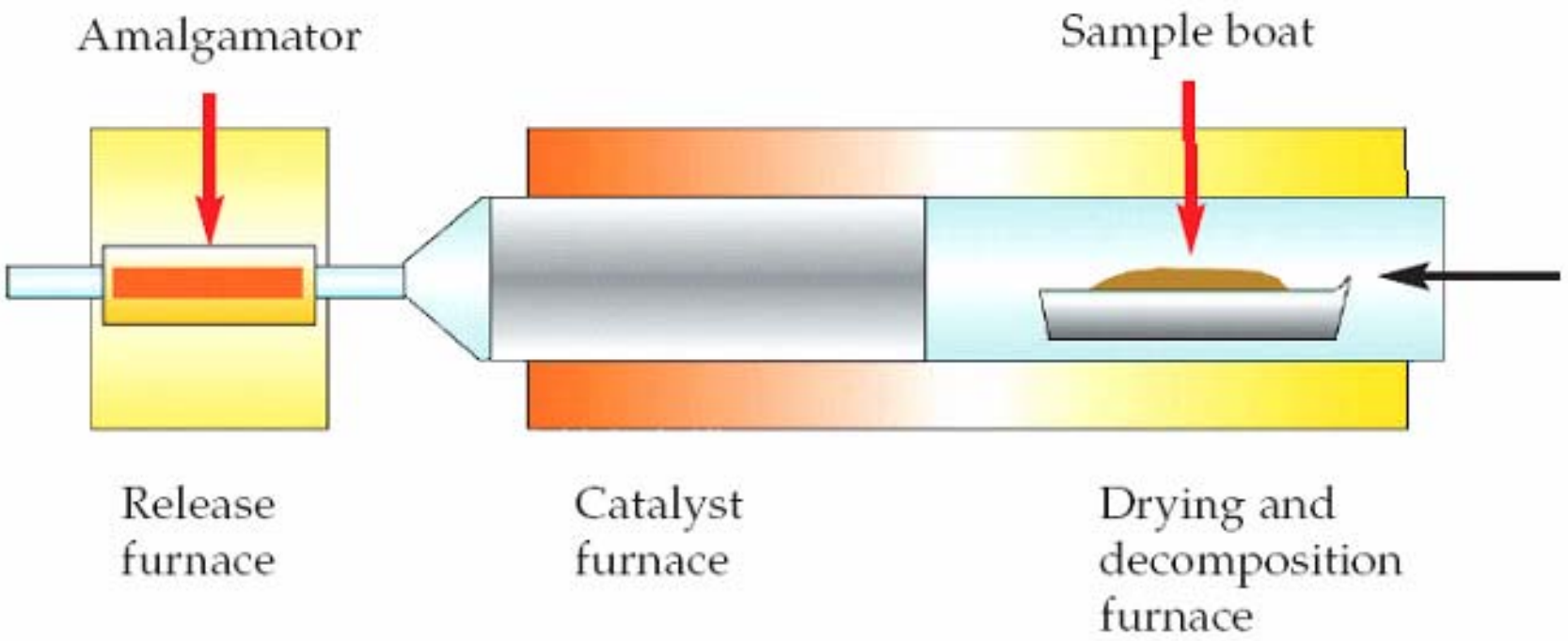


Fully Loaded Autosampler



Pipetting Liquid Samples

Thermal process



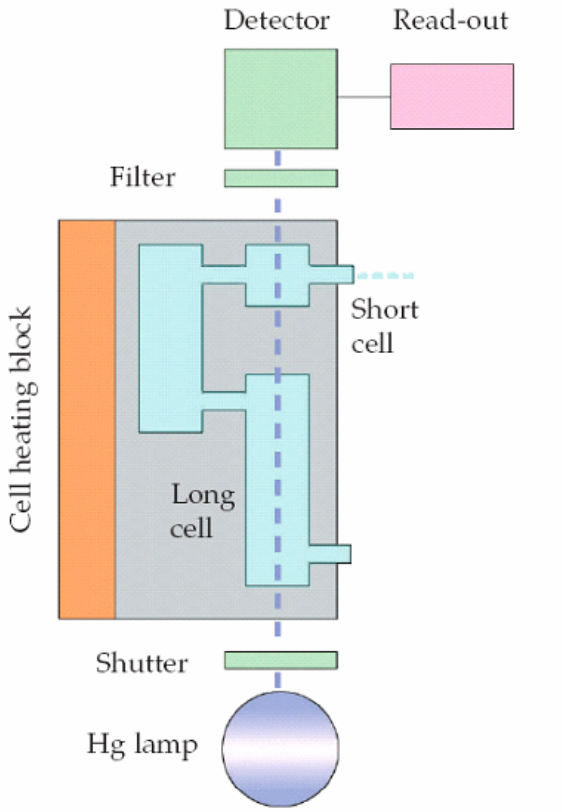
Thermal Process

Step	Temperature range	Typical temperature	Time range	Typical time
Drying	20-300°C	300°C	0-300 s	60 s
Decomposition	800-1.000°C	850°C	0-420 s	180 s
Catalysis	550-650°C	600°C		
Amalgam	850-950°C	900°C	0-30 s	12 s

Oxygen

Function	Carrier and decomposition gas
Inlet pressure	4 bar (60 psig)
Flow rate	200 ml/minute
Purity	“Research” grade (O_2 > 99,95%)

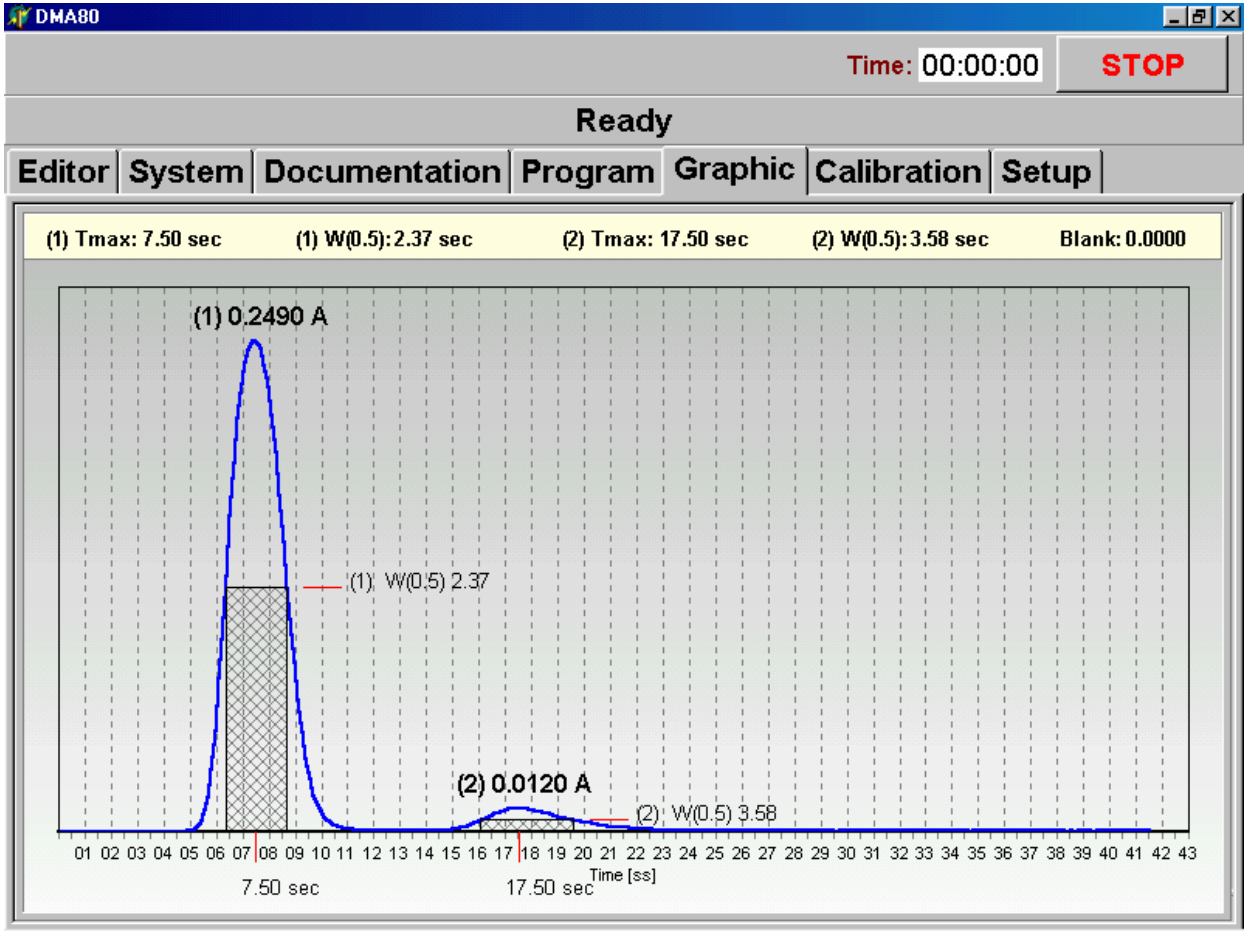
Atomic Absorption Spectrophotometer



AAS Technical Data

Instrument optics	Single beam spectrophotometer with sequential flow through of measurement cells
Light source	Low pressure mercury lamp
Wavelength	253,65 nm
Interference filter	254 nm, 9 nm bandwidth
Detector	Si-photodiode sensor

Typical Absorbance Profile



DMA-80
Performance Specifications

Data	Total Hg (ng)	Hg concentration[(1)] (μg/kg)
Working range[(2)]	(1st) 0,02-35 (2nd) 35-600	(1st) 0,2-350 (2nd) 350-6.000
Detection limit	0,02	0,2
[(1)]Sample weight 100 mg [(2)]Automatic switching when absorbance 0,8		

DMA-80
Performance Specifications

Typical reproducibility	< 1,5%
Typical analysis time	6 minutes

System controller

- Lab TERMINAL
  - Touch-screen Pentium-based controller, 266 MHz, 64 MB Ram, Windows 98, Color 12,1” TFT SVGA monitor, CD-ROM, FD, Smart Card Reader, 2 COM, 1 USB, LAN ports
- Standard bench-top computer with similar specifications
- Dedicated Terminal 1024

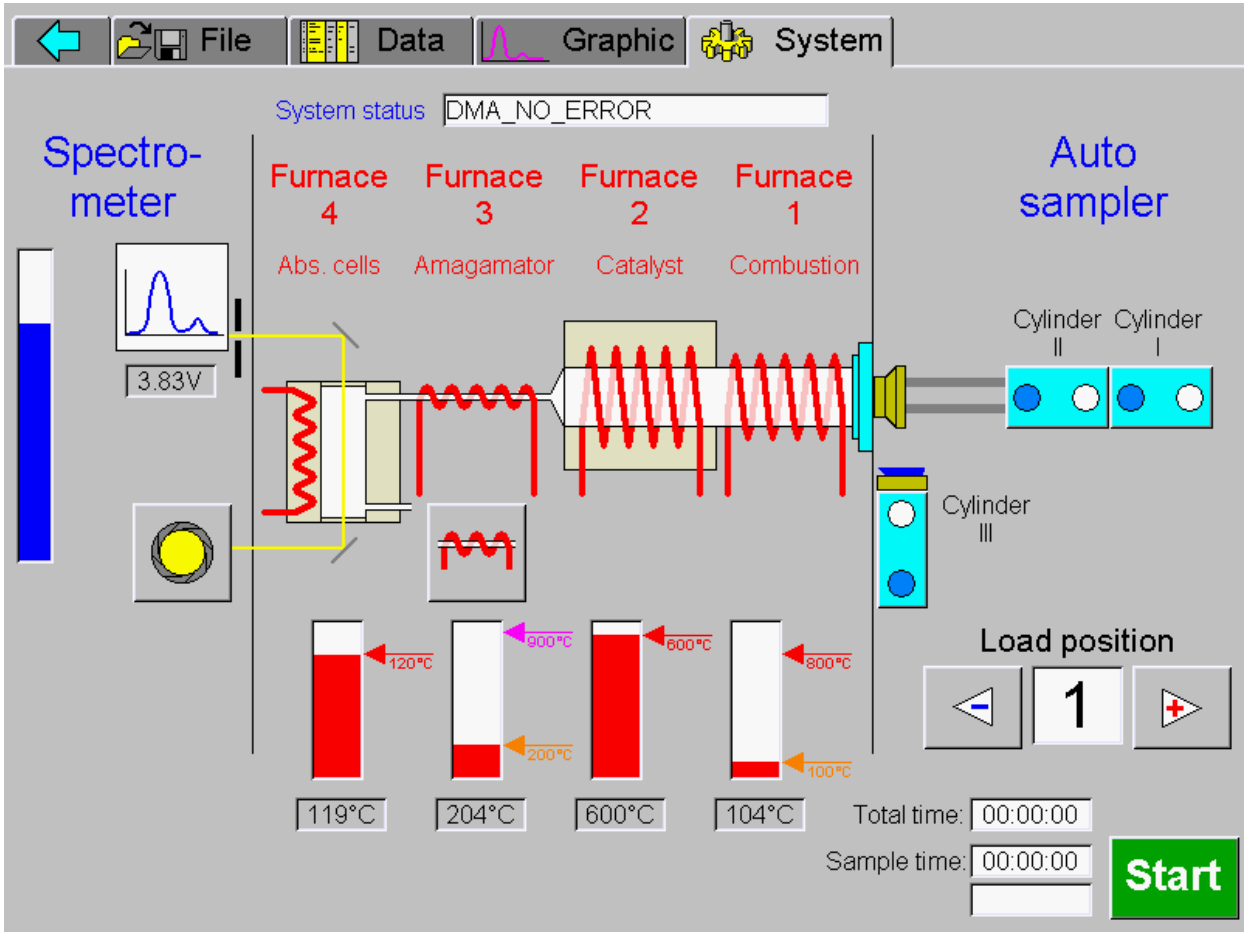
Terminal 1024

- 12” large high resolution color screen controller
- “Touch control” display
- Supplied with keyboard and mouse
- “EasyControl” software for a complete control of all reaction parameters
- Optional “EasyDoc” software for data export on external computer

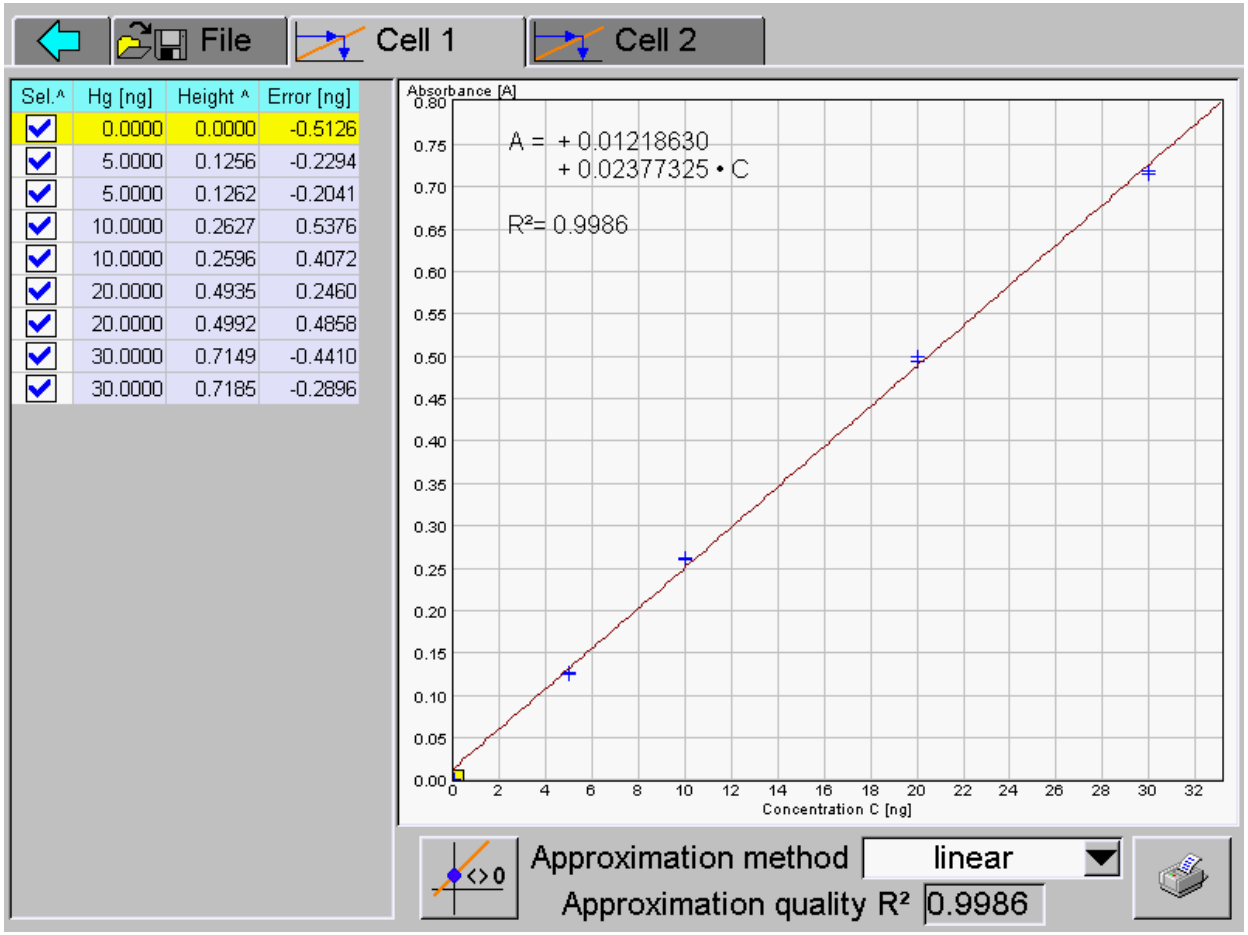
EasyControl Software

- Evolution of previous Windows™ based DMA-80 software
- Selectable calibration algorithm
- Virtually unlimited memory for programs and actual data storage
- Built-in service and diagnosis functions
- CFR-21 part 11 compliant

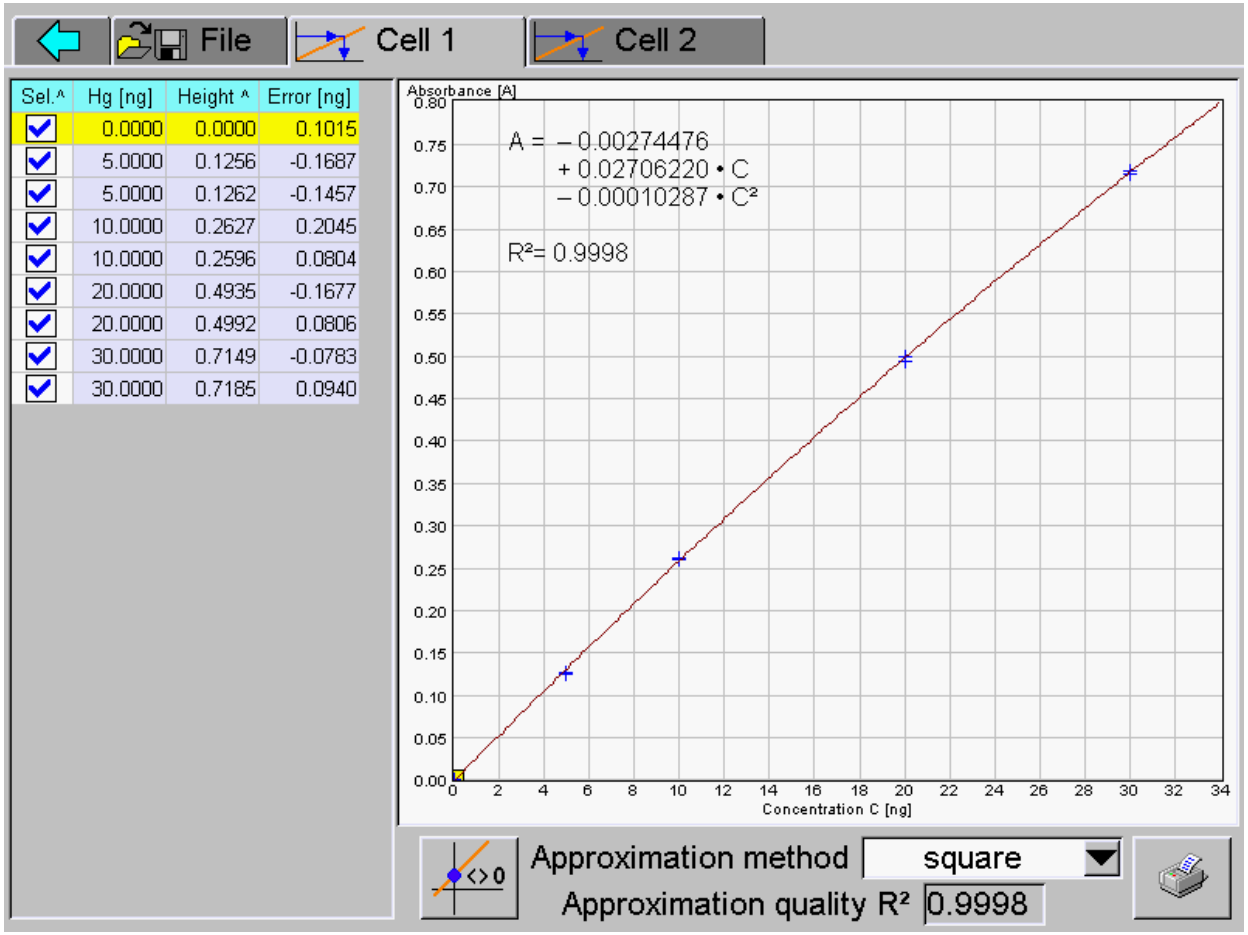
System Status



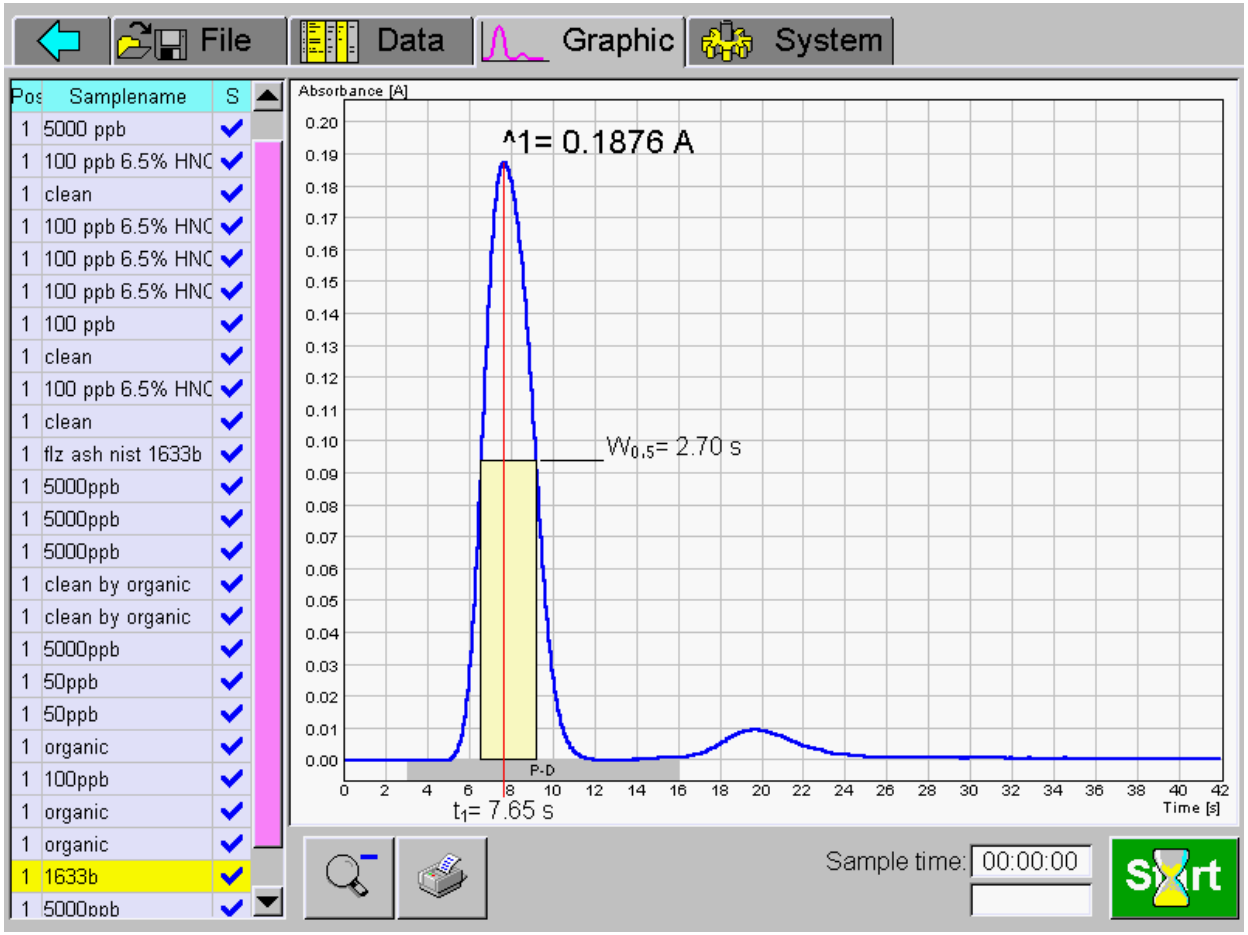
1st Cell Linear Calibration



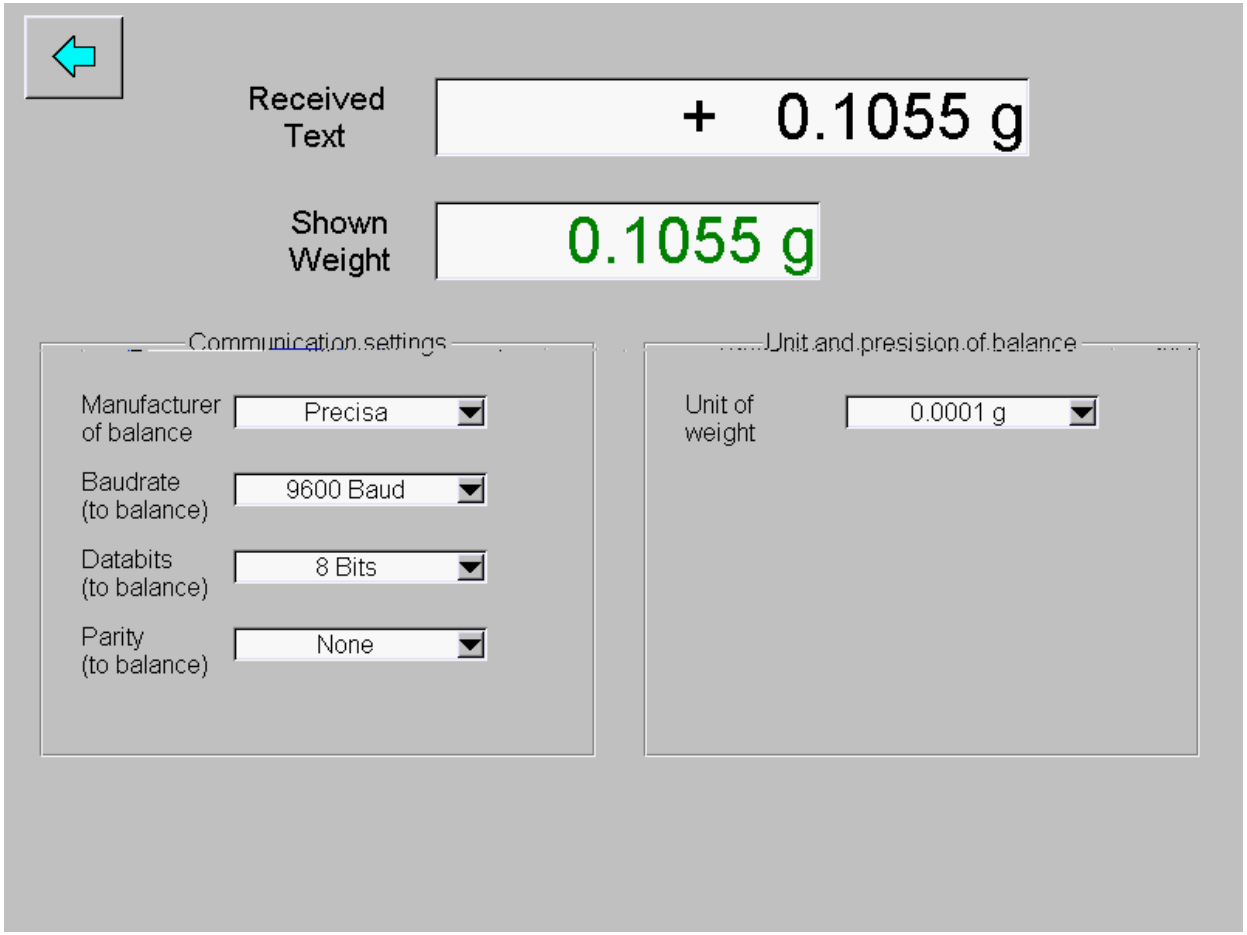
1st Cell Square Calibration



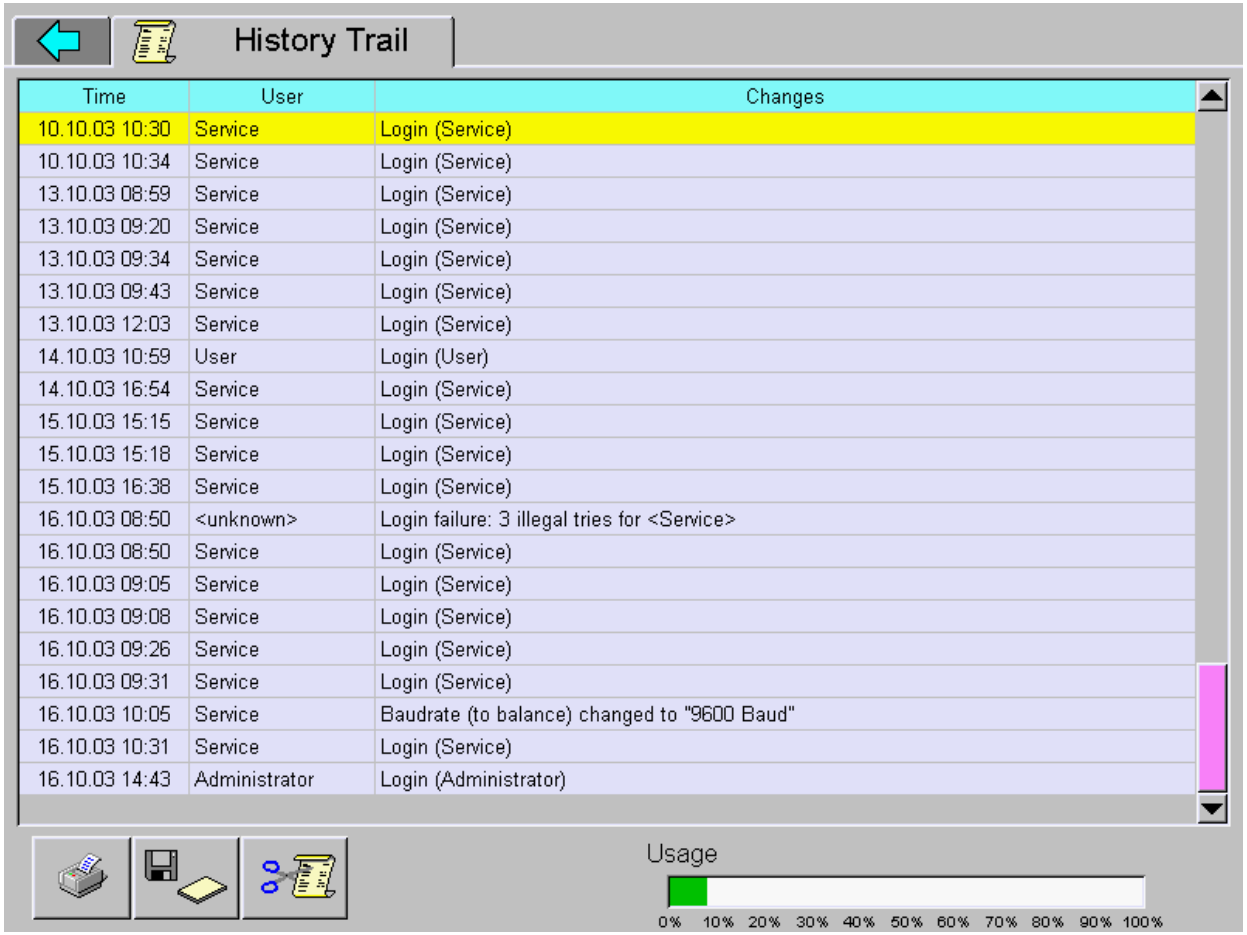
Measurement/Graphic



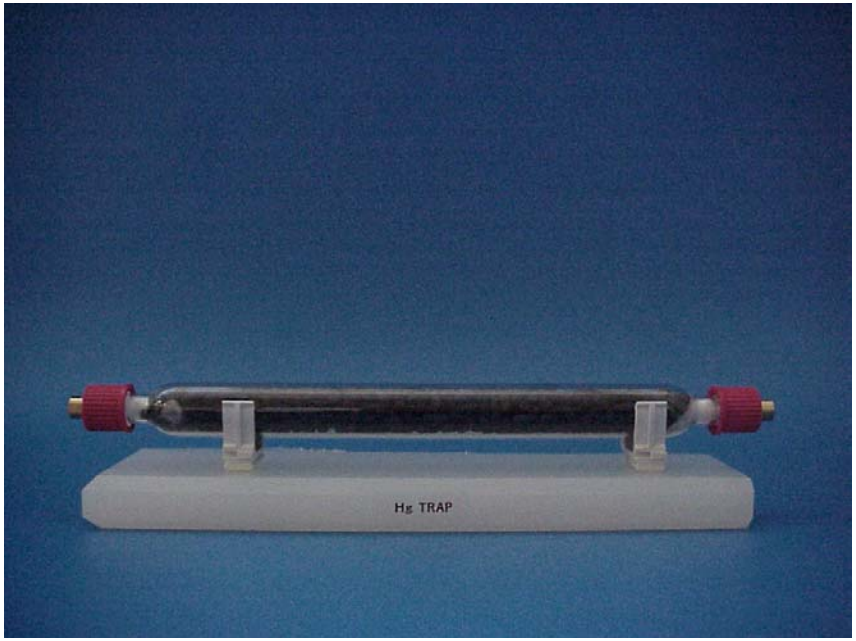
Balance Setup



History Trail CFR 21 Part 11



Mercury Trap



- Optional mercury trap to be located at DMA-80 outlet
- Activated charcoal
- Safe operation
- Easy and ready to install

DMA-80
Analytical Performance

Getting Started

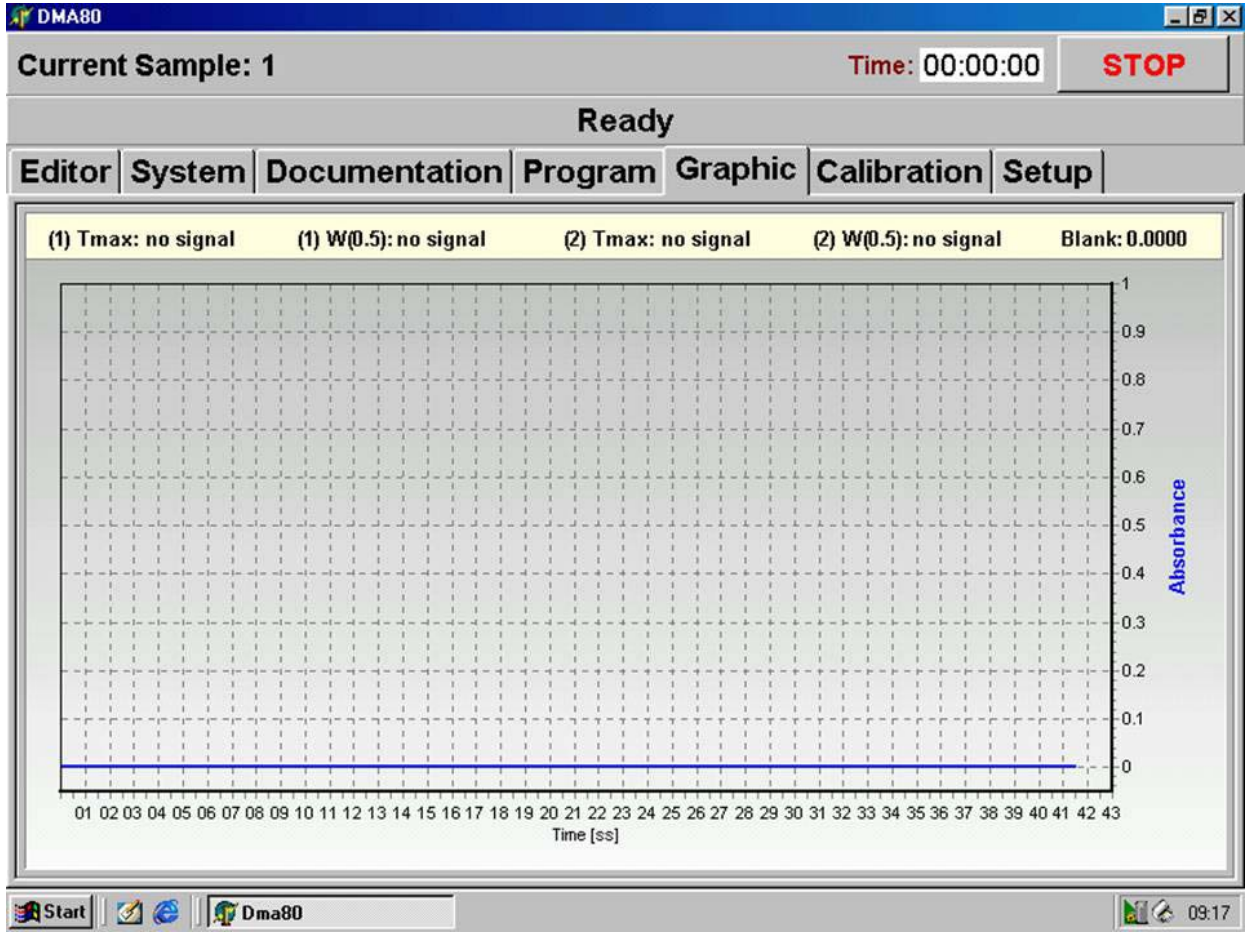
- Oxygen cylinder with gas regulator stable at 4 bar (60 psig)
- Power 115-230 V/50-60 Hz
- Analytical balance with serial interface
- Windows compatible printer
- Standard reference materials
- Aqueous standards
- Precision pipettes

DMA-80 Calibration

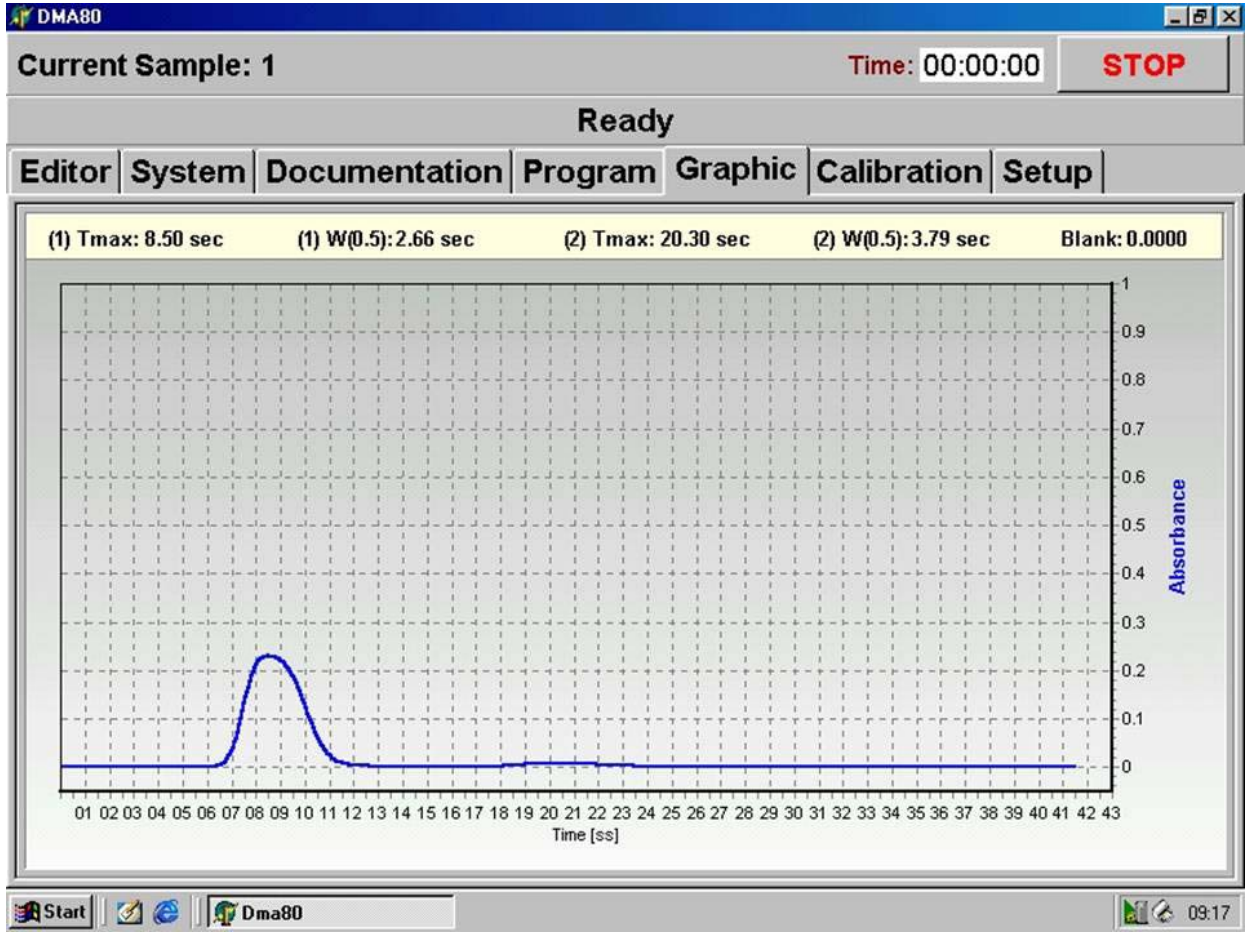
DMA-80 Calibration

- Liquid standards
  - Different concentrations, same volume
  - Same concentration, different volumes
  - Use fresh standards, stabilized with HNO_3 or $HCl/K_2Cr_2O_7$
- Solid standards
  - Certified mercury content
  - Vary by weight

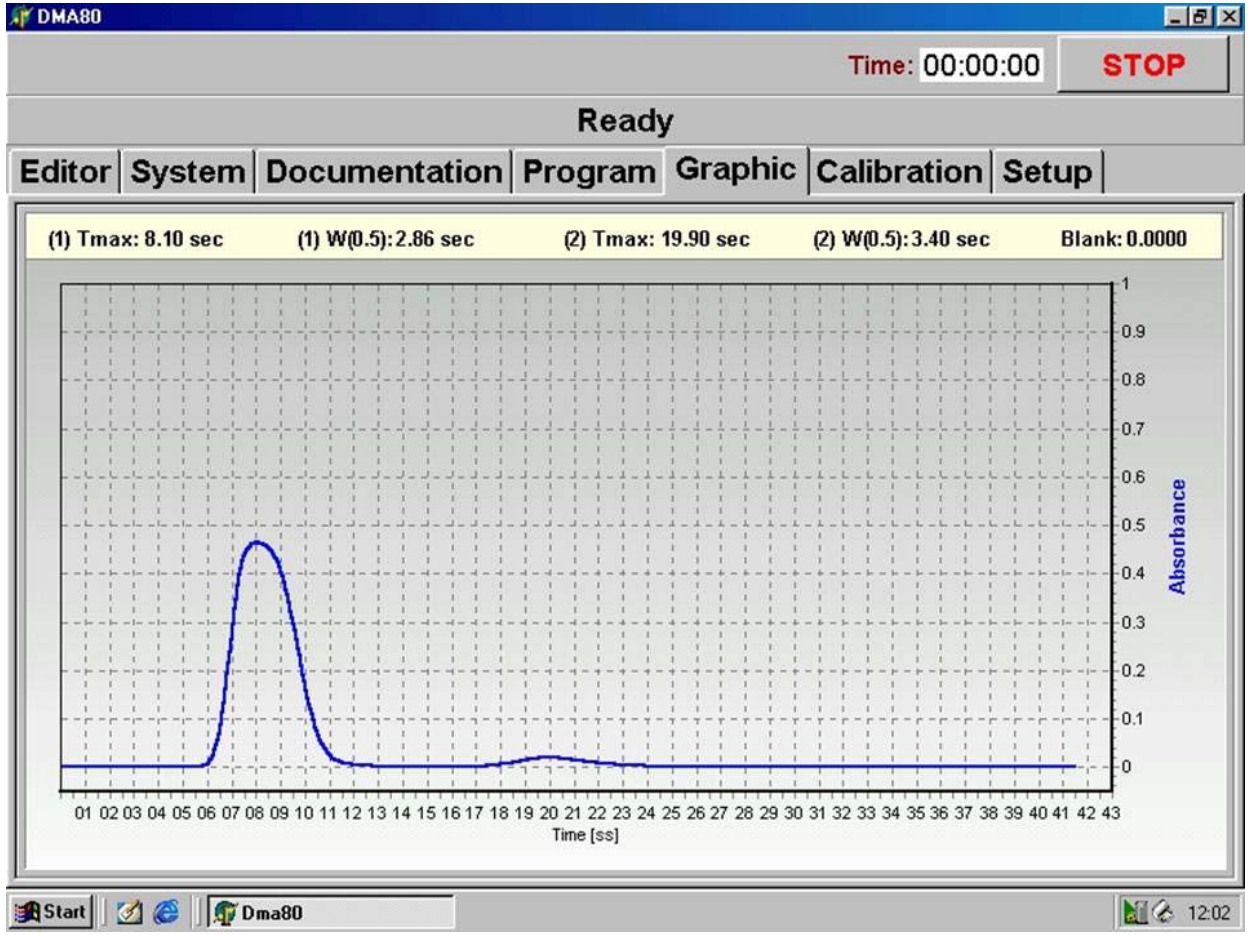
0 ng


DMA80
Current Sample: 1
Time: 00:00:00
STOP
Ready
Editor
System
Documentation
Program
Graphic
Calibration
Setup
(1) Tmax: no signal
(1) W(0.5): no signal
(2) Tmax: no signal
(2) W(0.5): no signal
Blank: 0.0000
Absorbance
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
01 02 03 04 05 06 07 08 09 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43
Time [ss]
Start
Dma80
09:17

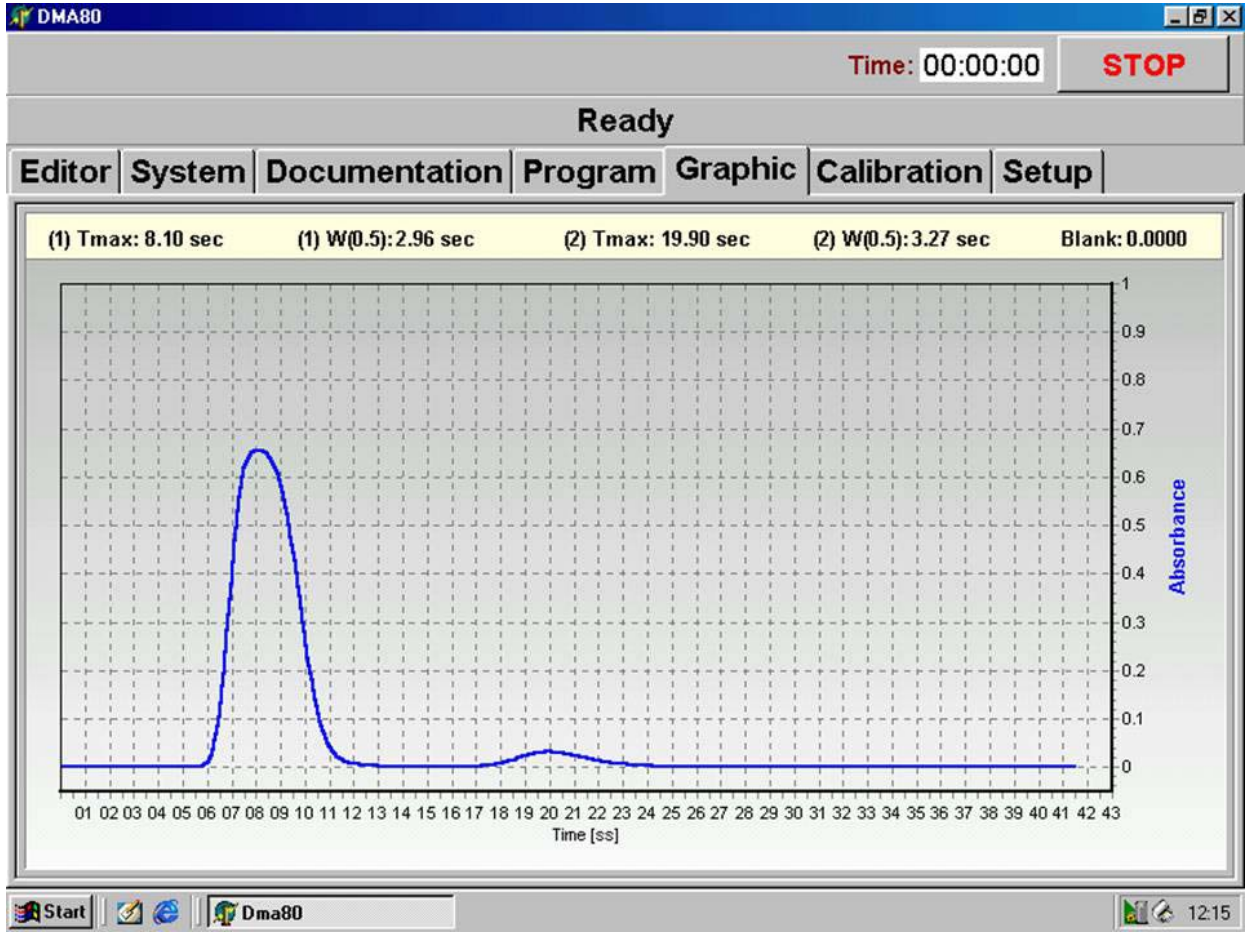
10 ng


DMA80
Current Sample: 1
Time: 00:00:00
STOP
Ready
Editor
System
Documentation
Program
Graphic
Calibration
Setup
(1) Tmax: 8.50 sec
(1) W(0.5): 2.66 sec
(2) Tmax: 20.30 sec
(2) W(0.5): 3.79 sec
Blank: 0.0000
Absorbance
Time [ss]
Start
Dma80
09:17

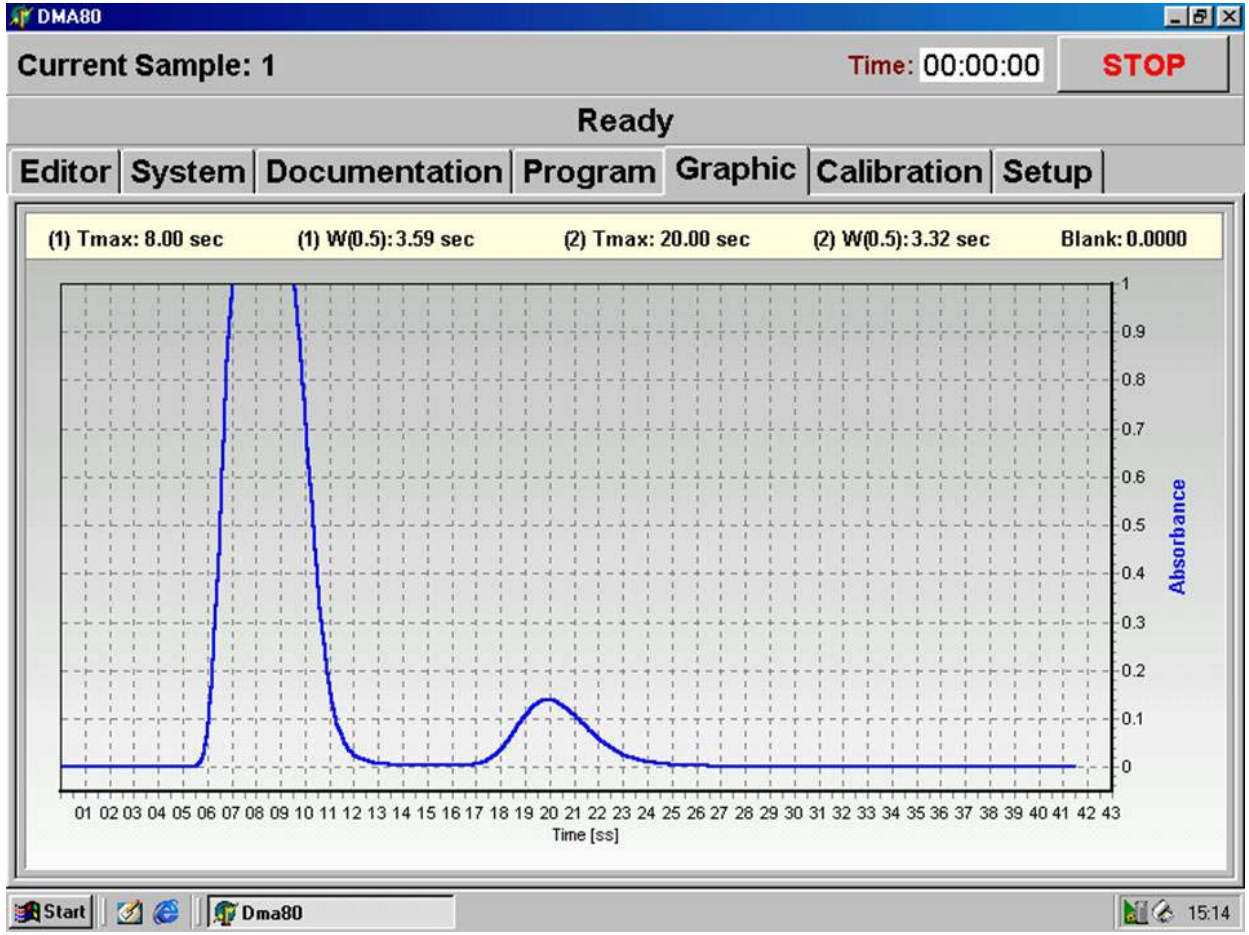
20 ng


DMA80
Time: 00:00:00
STOP
Ready
Editor
System
Documentation
Program
Graphic
Calibration
Setup
(1) Tmax: 8.10 sec
(1) W(0.5): 2.86 sec
(2) Tmax: 19.90 sec
(2) W(0.5): 3.40 sec
Blank: 0.0000
Absorbance
Time [ss]
Start
Dma80
12:02

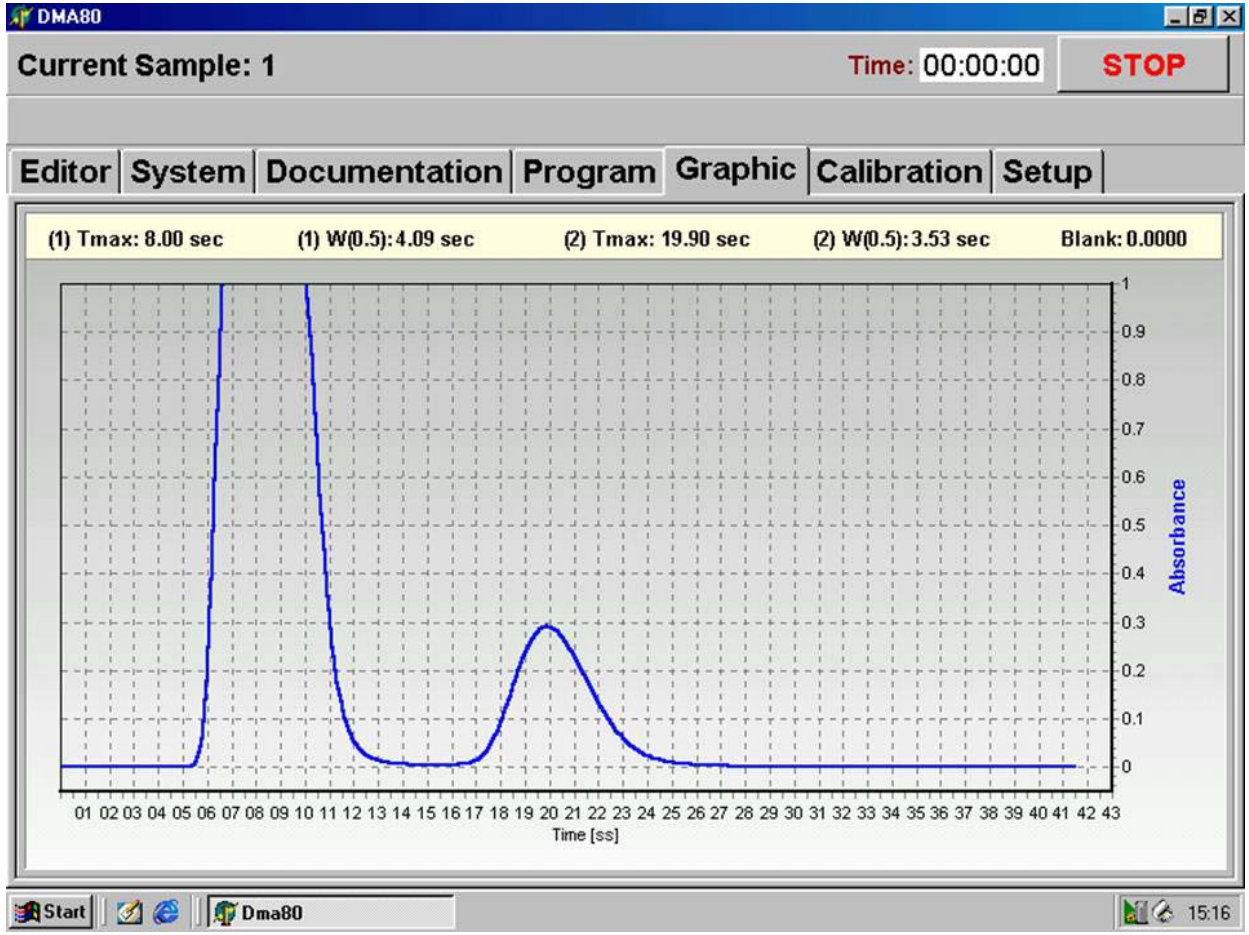
30 ng


DMA80
Time: 00:00:00
STOP
Ready
Editor
System
Documentation
Program
Graphic
Calibration
Setup
(1) Tmax: 8.10 sec
(1) W(0.5): 2.96 sec
(2) Tmax: 19.90 sec
(2) W(0.5): 3.27 sec
Blank: 0.0000
Absorbance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
01 02 03 04 05 06 07 08 09 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43
Time [ss]
Start
Dma80
12:15

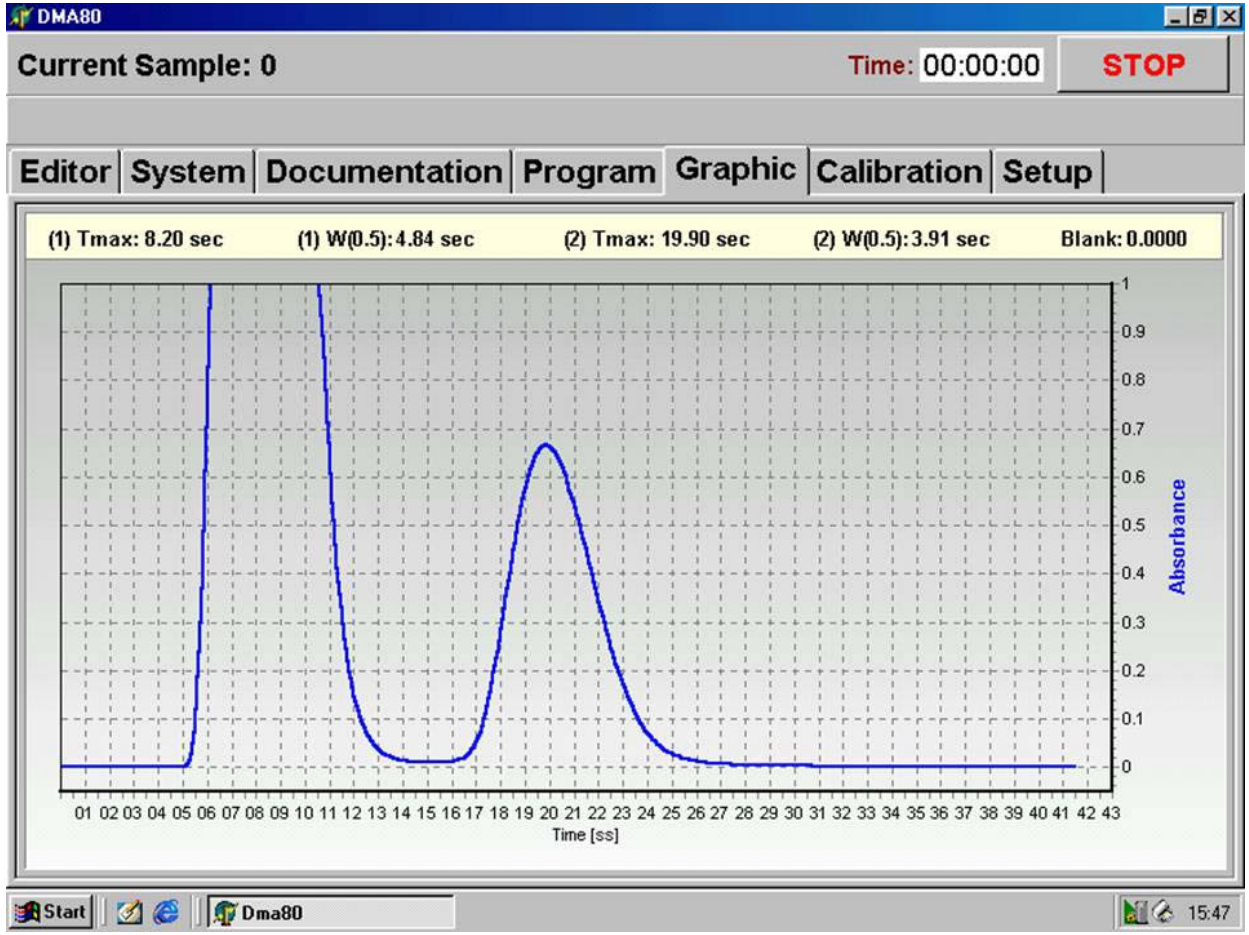
100 ng


DMA80
Current Sample: 1
Time: 00:00:00
STOP
Ready
Editor
System
Documentation
Program
Graphic
Calibration
Setup
(1) Tmax: 8.00 sec
(1) W(0.5): 3.59 sec
(2) Tmax: 20.00 sec
(2) W(0.5): 3.32 sec
Blank: 0.0000
Absorbance
Time [ss]
Start
Dma80
15:14

200 ng


DMA80
Current Sample: 1
Time: 00:00:00
STOP
Editor
System
Documentation
Program
Graphic
Calibration
Setup
(1) Tmax: 8.00 sec
(1) W(0.5): 4.09 sec
(2) Tmax: 19.90 sec
(2) W(0.5): 3.53 sec
Blank: 0.0000
Absorbance
Time [ss]
Start
Dma80
15:16

500 ng


DMA80
Current Sample: 0
Time: 00:00:00
STOP
Editor
System
Documentation
Program
Graphic
Calibration
Setup
(1) Tmax: 8.20 sec
(1) W(0.5): 4.84 sec
(2) Tmax: 19.90 sec
(2) W(0.5): 3.91 sec
Blank: 0.0000
Absorbance
Time [ss]
Start
Dma80
15:47

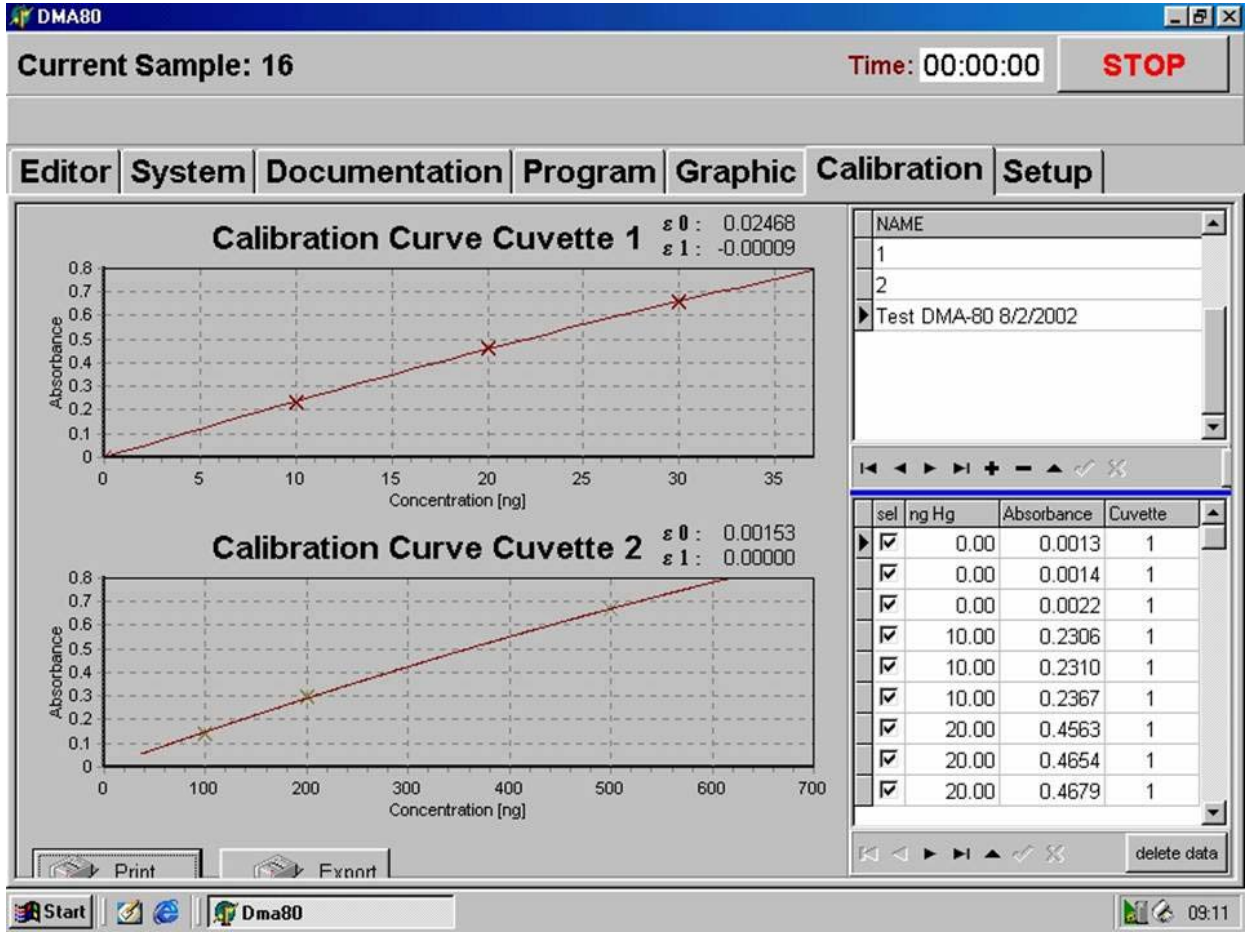
Calibration 1st Cell

Solution	Absorbance	RSD (n=3)
Blank	0,0012	16,7%
5 ng	0,1272	1,5%
10 ng	0,2549	2,2%
20 ng	0,4996	1,2%
30 ng	0,7223	0,6%

Calibration 2nd Cell

Solution	Absorbance	RSD (n=3)
100 ng	0,1546	2,2%
200 ng	0,3117	1,9%
500 ng	0,7285	0,9%

Calibration Curves

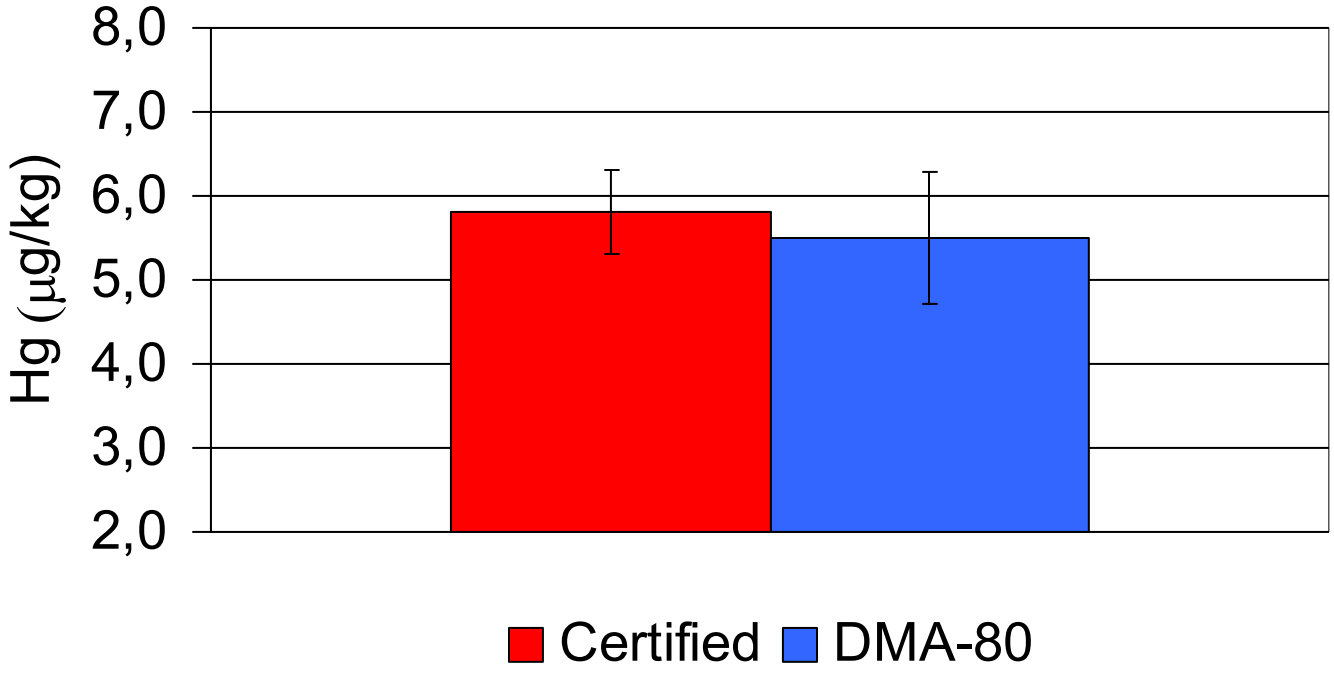


DMA-80 Accuracy

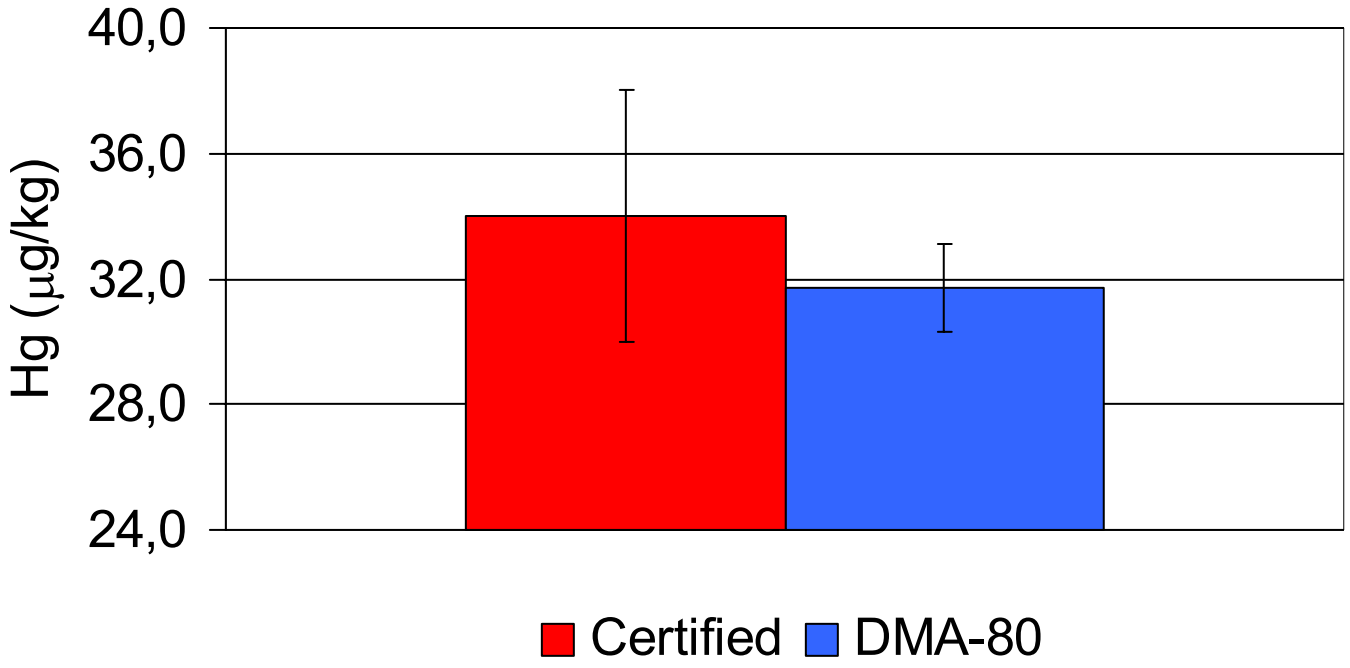
Certified Reference Materials

Sample	Hg content (μg/kg)
NIST 1568a Rice Flour	5,8 ± 0,5
NIST 1573a Tomato Leaves	34 ± 4
NIST 1630a Coal	93,8 ± 3,7
NIST 1633b Fly Ash	141 ± 19
NIST 2709 Soil	1.400 ± 80
NIST 2711 Soil	6.250 ± 190

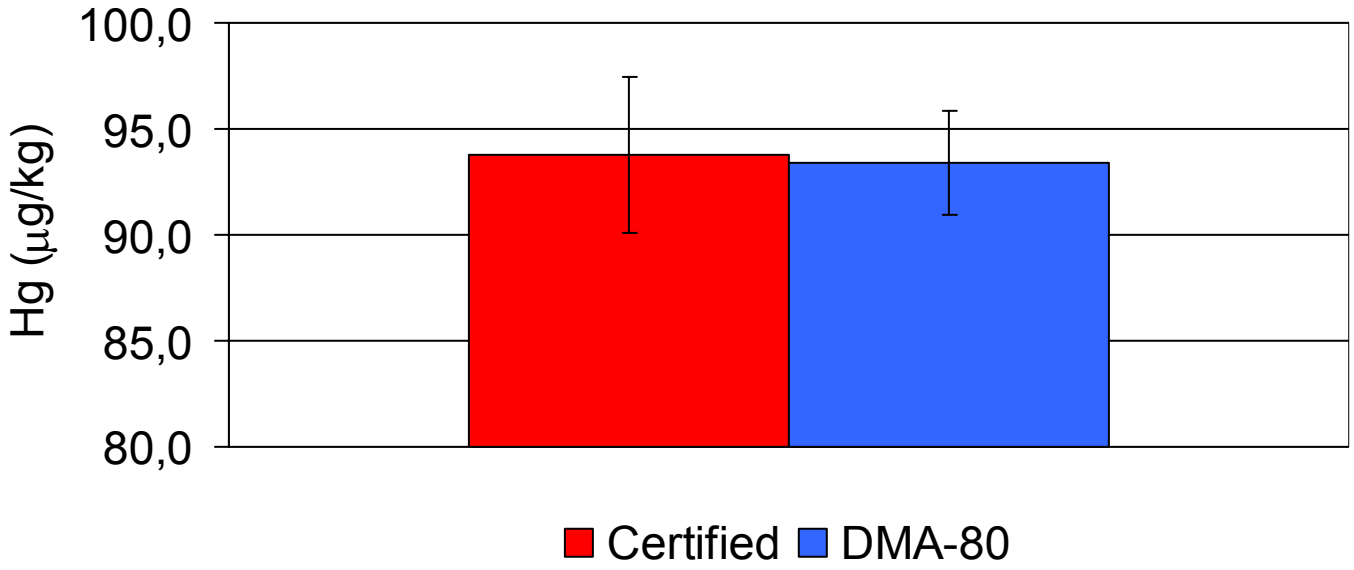
NIST 1568a Rice Flour



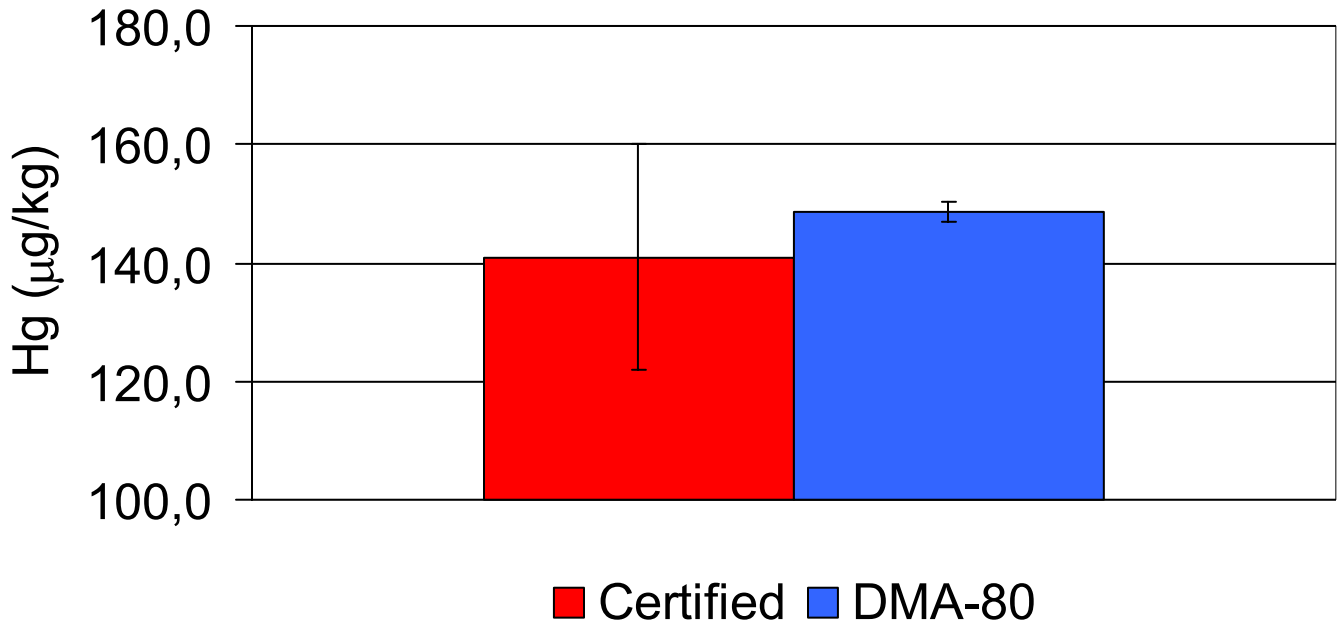
NIST 1573a Tomato Leaves



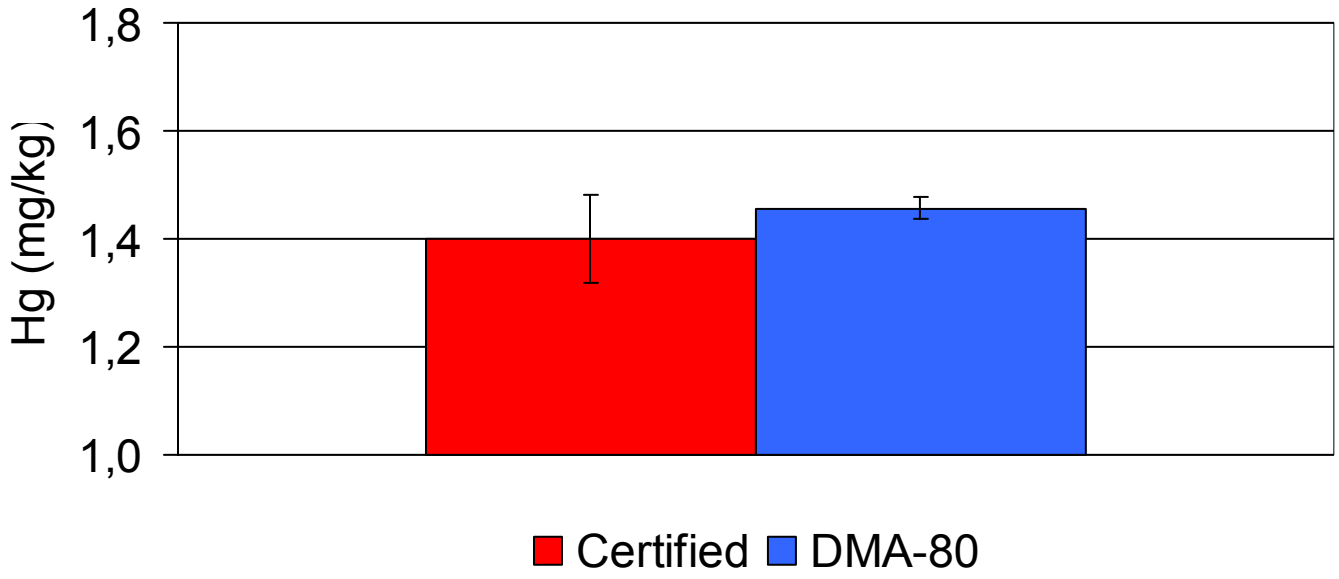
NIST 1630a Coal



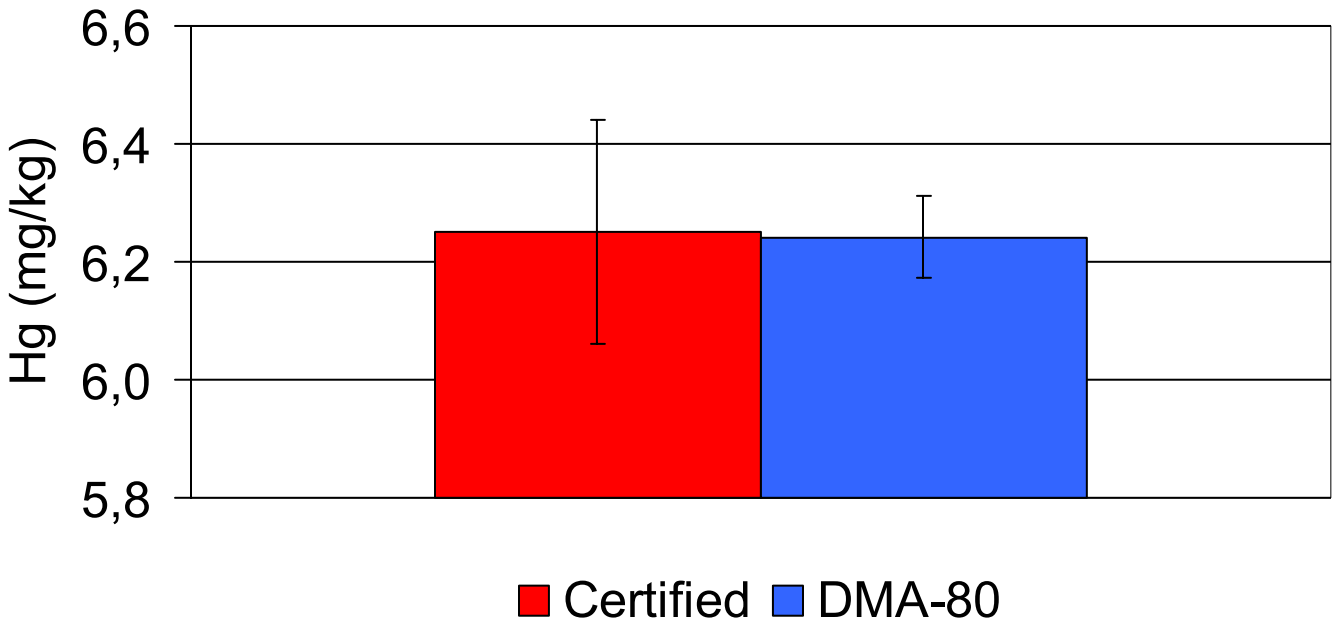
NIST 1633b Fly Ash



NIST 2709 Soil



NIST 2711 Soil



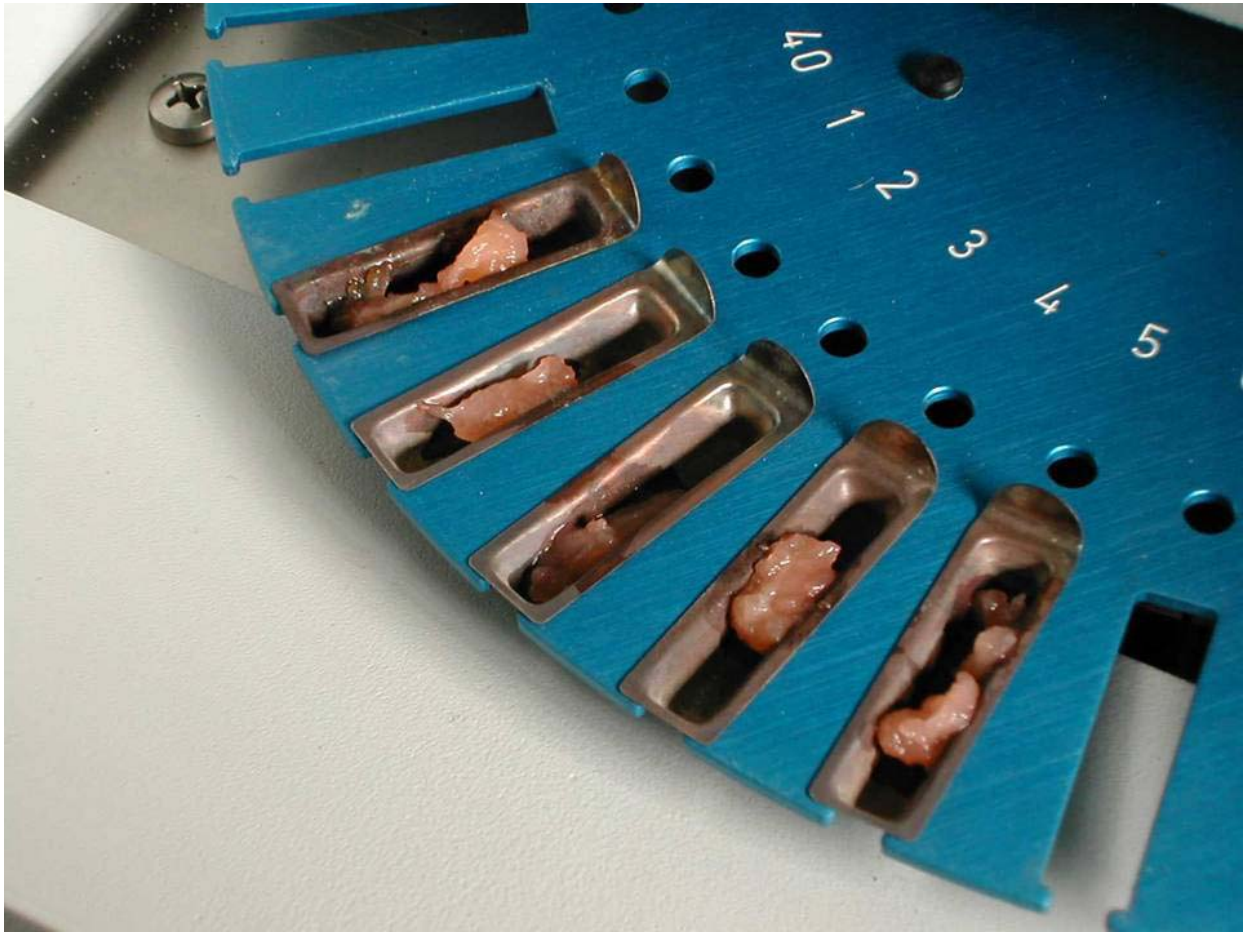
DMA-80 Precision

Fresh Salmon

Collecting Sample

Weighing

Loading Autosampler



Loading Furnace

After Analysis

Fresh Salmon

Run	Weight (g)	Hg (μg/kg)
1	0,2849	55,4
2	0,2296	54,1
3	0,2330	57,8
4	0,3404	58,0
5	0,2992	56,2

Fresh Salmon

Average (μg/kg)	56,3
Sd (μg/kg)	1,6
N	5

DMA-80 Detection Limit

Detection Limit

The detection limit is defined as the concentration which will give an absorbance signal of two (sometimes three) times the magnitude of the baseline noise. The baseline noise may be statistically quantified typically by making ten or more replicate measurements of the baseline absorbance signal observed for an analytical blank, and determining the standard deviation of the measurements. The detection limit is then defined as the concentration which will produce an absorbance signal twice (or three times) the standard deviation

Detection Limit

Run	Absorbance	Run	Absorbance
1	0,0007	6	0,0010
2	0,0010	7	0,0008
3	0,0006	8	0,0010
4	0,0008	9	0,0008
5	0,0007	10	0,0006

Detection Limit

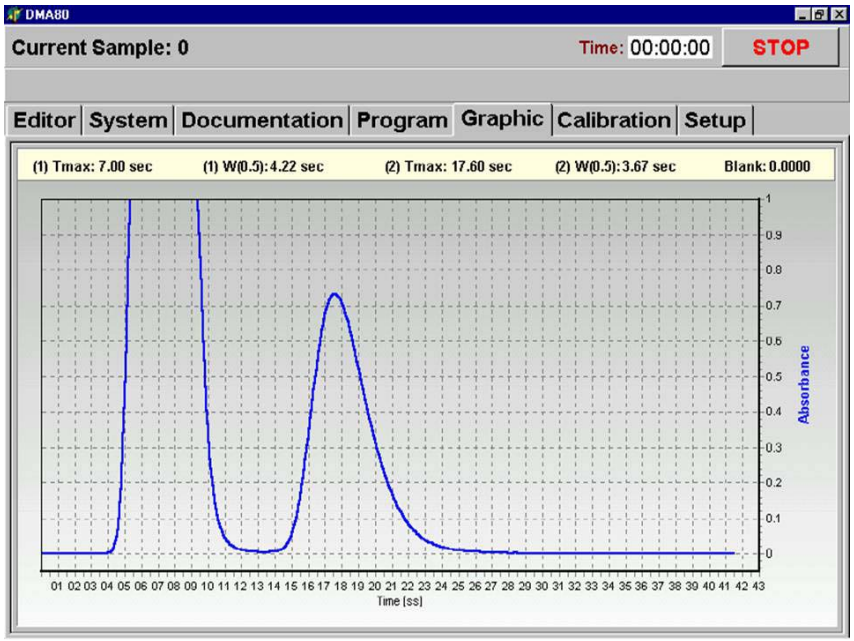
Average	0,0008
Sd	0,000156
3*Sd	0,000468
DL	0,02 ng

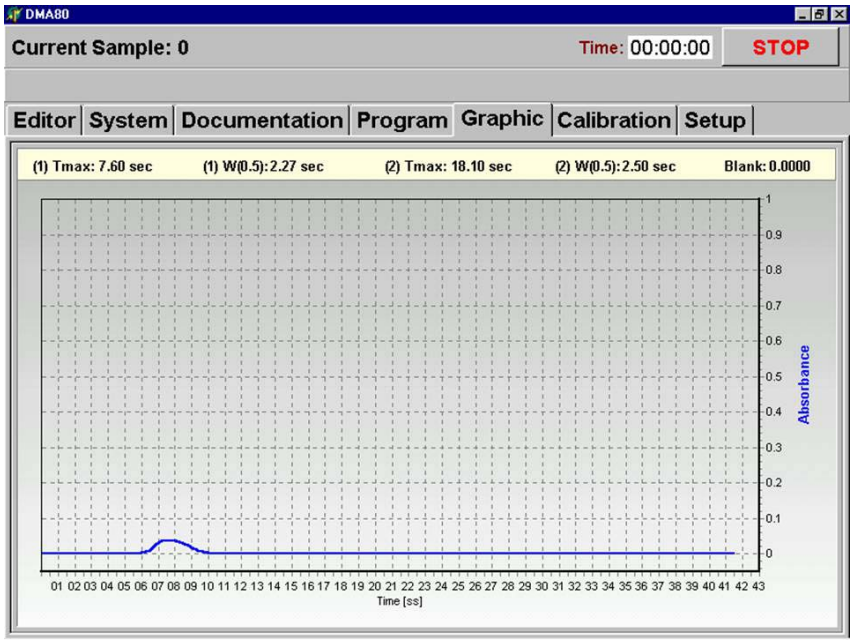
DMA-80 Memory Effect

DMA-80 Memory Effect

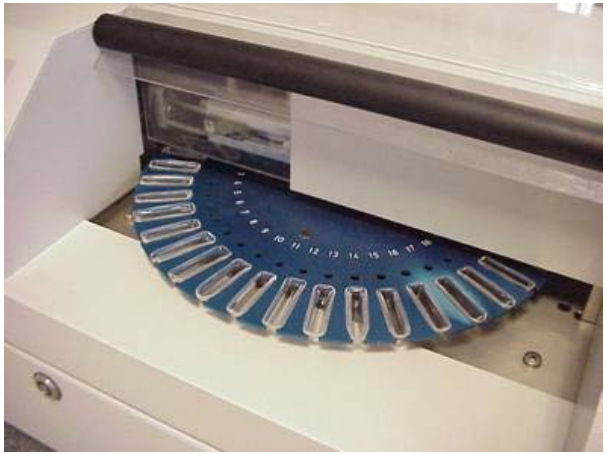
Sample	Absorbance	Mercury content (ng)
Standard 500 ng	0,7285 (2^{nd})	500 (set)
Blank 1	0,0374 (1^{st})	1,5
Blank 2	0,0097 (1^{st})	0,4

DMA-80 Memory Effect



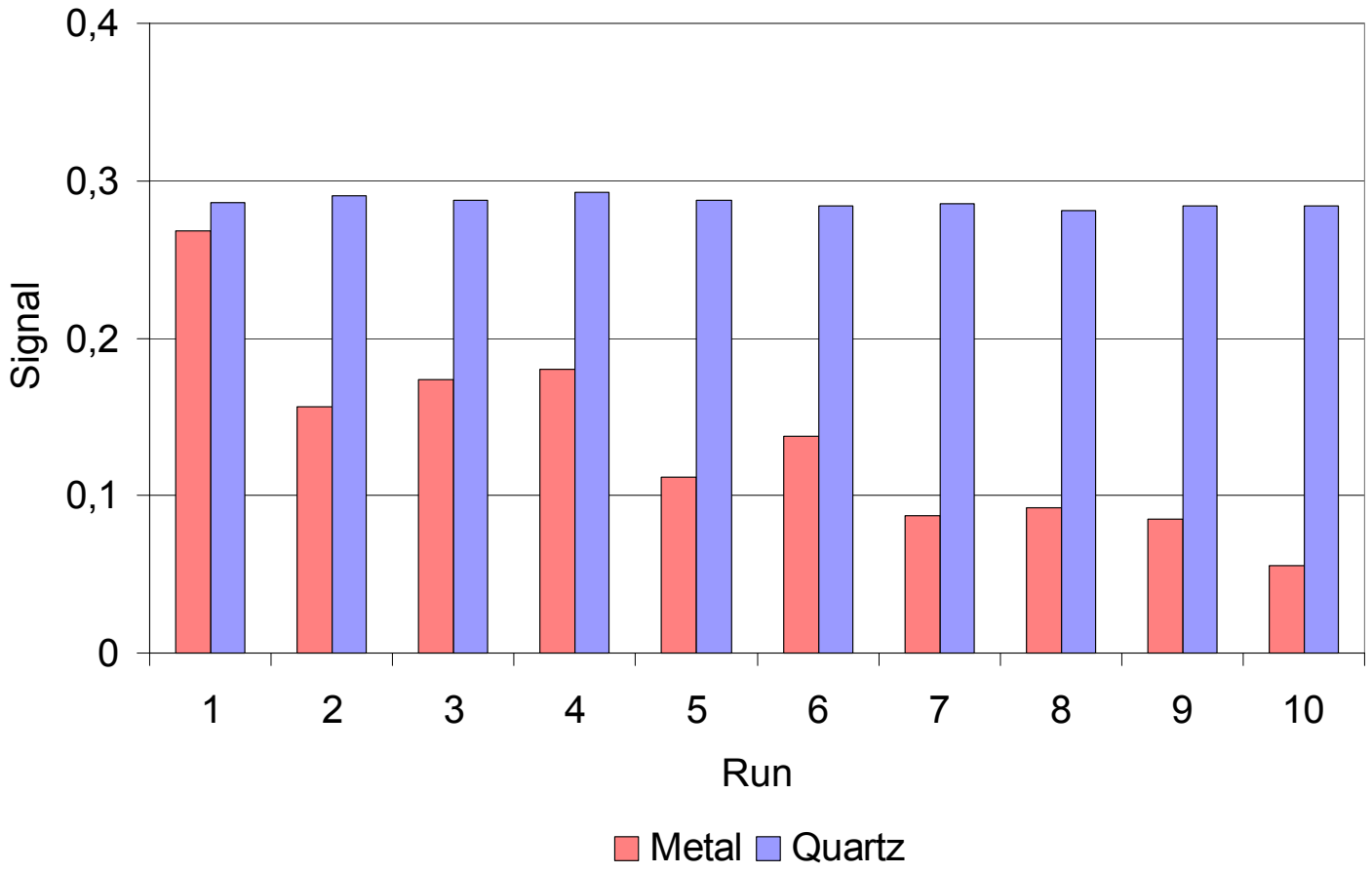


Quartz Boats



- Analysis of liquids with DMA-80 autosampler
- Improved performance
  - Lower memory effect
  - Better reproducibility
- Longer life time

Quartz vs. Metal Boats



Memory Effect

Sample ID	Weight (g)	Height	Hg (ng)	Result (µg/kg)
1	0,100	0,1474	110,60	1.106,01
1	0,100	0,0011	0,05	0,45
1	0,100	0,000	0,00	0,01

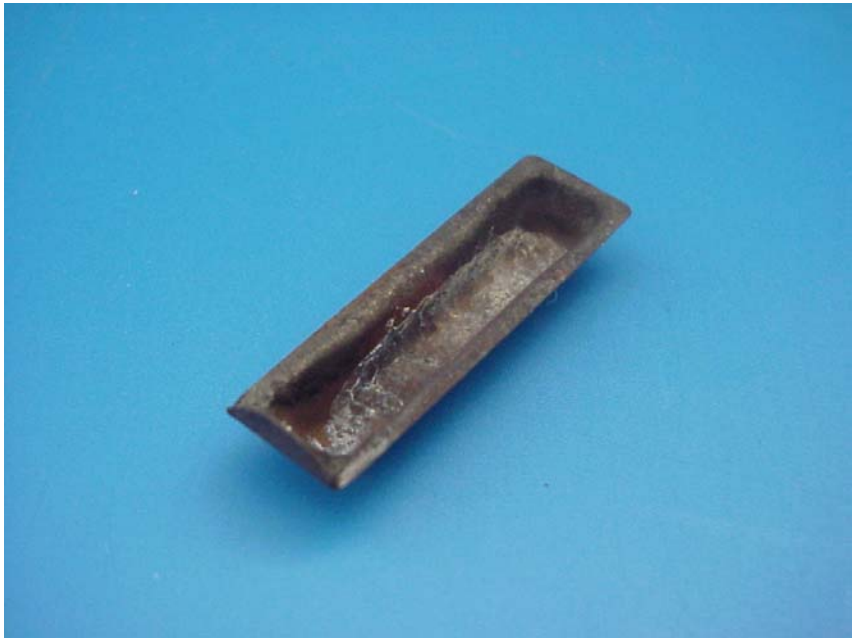
Reproducibility at Low Concentrations

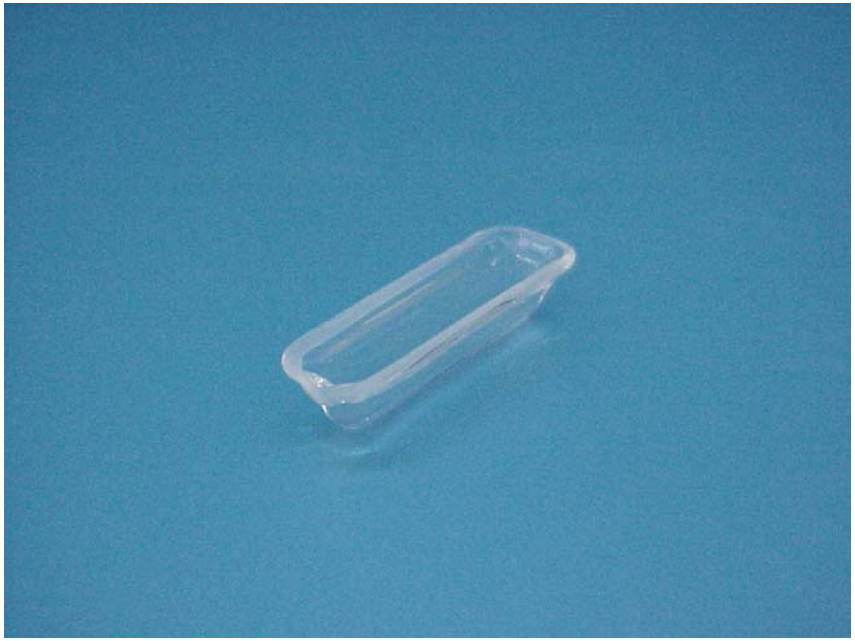
Weight (g)	Height	Hg (ng)	Results (μg/kg)
0,100	0,0222	0,87	8,72
0,100	0,0218	0,85	8,53
0,100	0,0217	0,85	8,51
0,100	0,0216	0,85	8,49
0,100	0,0217	0,85	8,50
Statistics	RSD 1,01%	SD 0,09 μg/kg	AVG 8,55

Reproducibility at High Concentrations

Weight (g)	Height	Hg (ng)	Results (µg/kg)
0,100	0,1517	113,88	1.138,8
0,100	0,1514	113,62	1.136,2
0,100	0,1520	114,13	1.141,3
0,100	0,1543	115,87	1.158,7
0,100	0,1523	114,34	1.143,4
Statistics	SD 7,88 µg/kg	RSD 0,69%	AVG 1.143,7

Lifetime





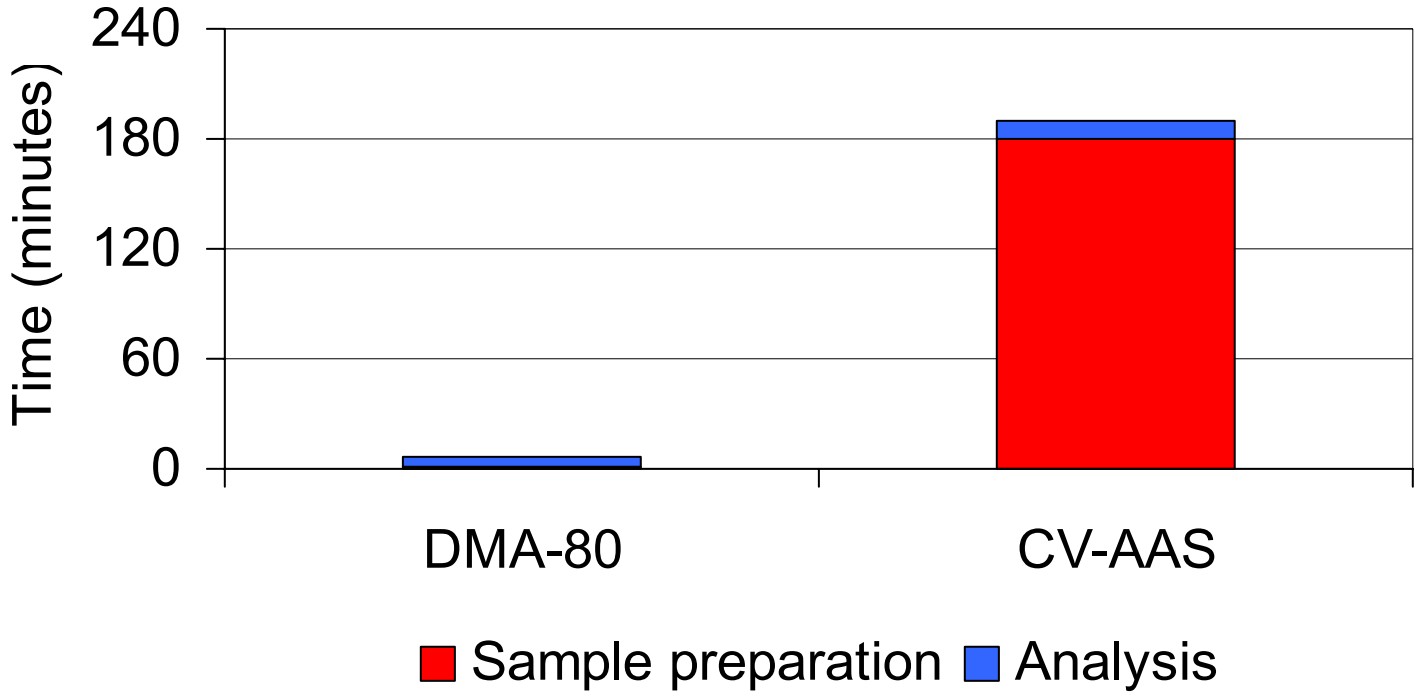
- US EPA method 7473
  - Mercury in solids and solutions by thermal decomposition amalgamation and atomic absorption spectrophotometry

Comparison
DMA-80 vs. CV-AAS

Comparison
DMA-80 vs. CV-AAS

Technique	DMA-80	CV-AAS
Sample preparation	Not required	Acid digestion
Wet chemistry	Not required	Yes, to eliminate interferences
Waste generation	Minimal	Yes
Sample type	Liquid and solids	Aqueous
Sample size	Up to 500 mg sample	100 ml solution
Working range	Up to 600 ng	Limited to low range
Running cost	Moderate	Elevated

Time Comparison
DMA-80 vs. CV-AAS



DMA-80 Major Applications

- Biological
  - Blood, urine, hair, tissue, plankton
- Liquids
  - Waste water, crude oil, heavy oil, detergents, paints
- Solids
  - Coal, fly ash, soil, sediment, sludge, minerals, food, feed, plastic, wood, vegetables, leaves, waxes
- Medicinal
  - Pharmaceuticals, gelatin capsules, lipstick, lotions

DMA-80
Direct Mercury Analyzer