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Exploiting the multicommutation approach for calibration using a single standard solution: application to the determination of mercury by CVAAS

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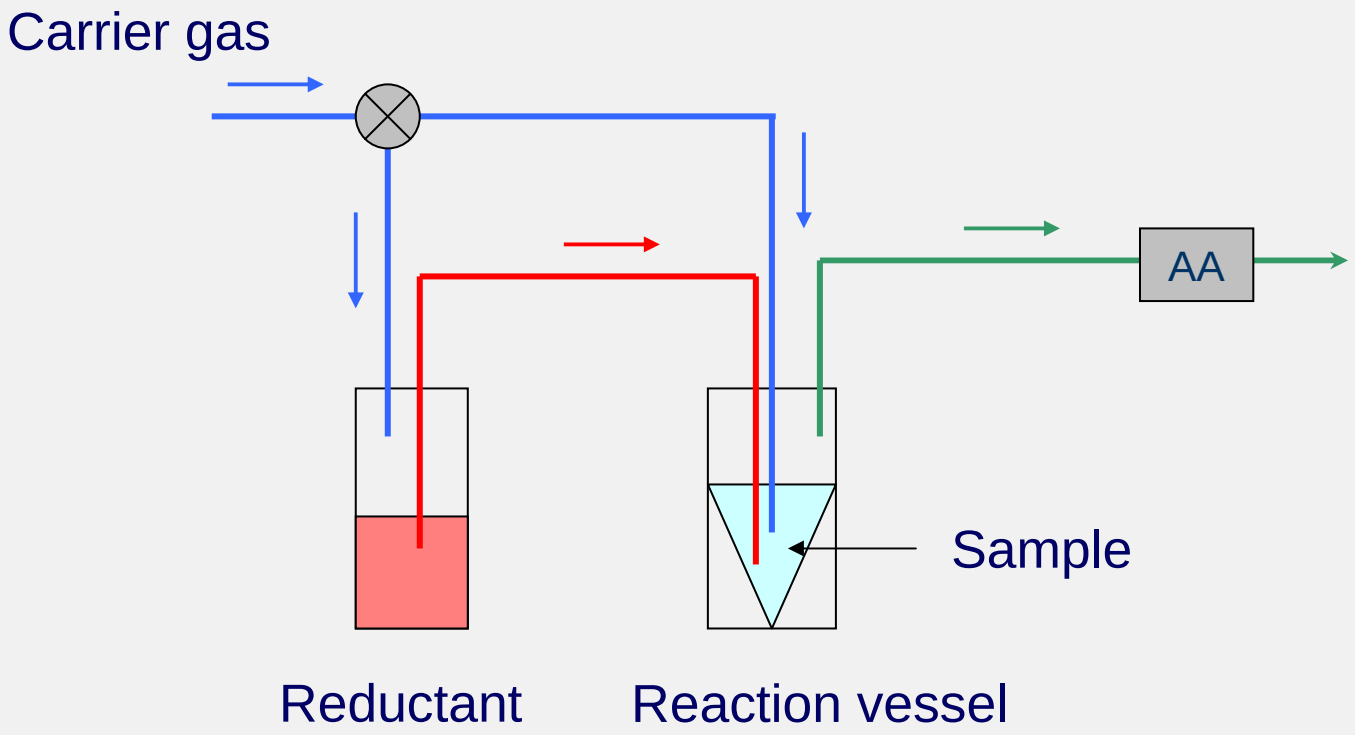
- Hatch and Ott, Anal. Chem. 40 (1968)
- Standard method for Hg determination (EN 13806, AOAC)

$$Hg(II) \xrightarrow[\text{Reductant}\ (Sn^{2+};\ BH_4^-)]{} Hg_0 \xrightarrow[\text{Carrier gas}\ (Ar;\ N_2)]{} AAS\ (\lambda=253.7\ nm)$$

- Batch systems
- Flow systems

CVAAS - Batch system



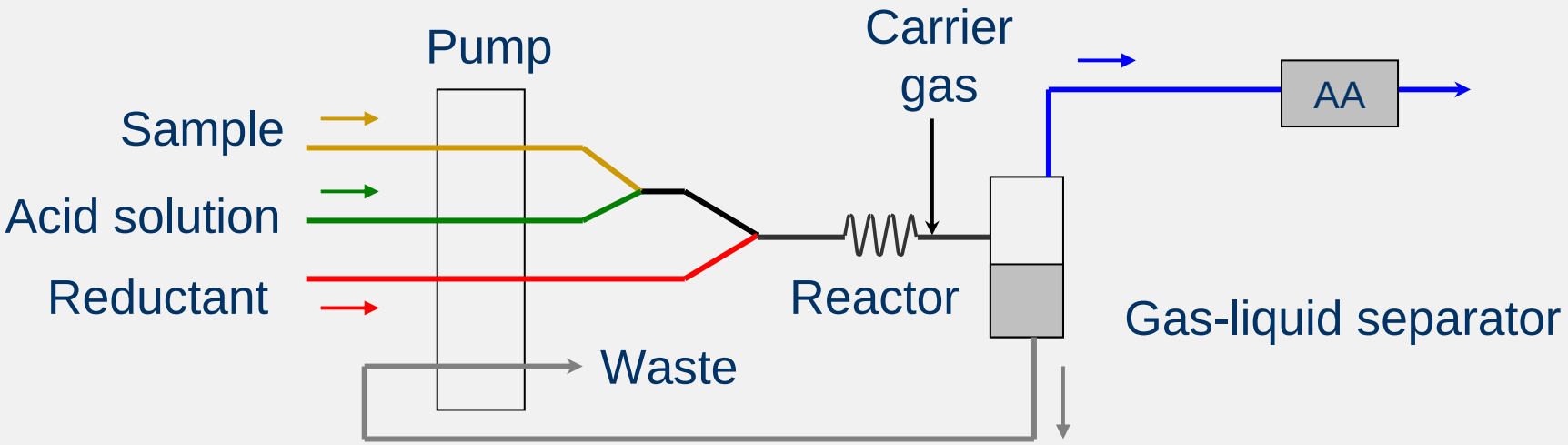
Limitations

- high reagent/sample consumption
- time consumption

- Batch systems
- Flow systems
  - Segmented flow analysis (SFA)
  - Continuous sample flow

CVAAS - Continuous sample flow system

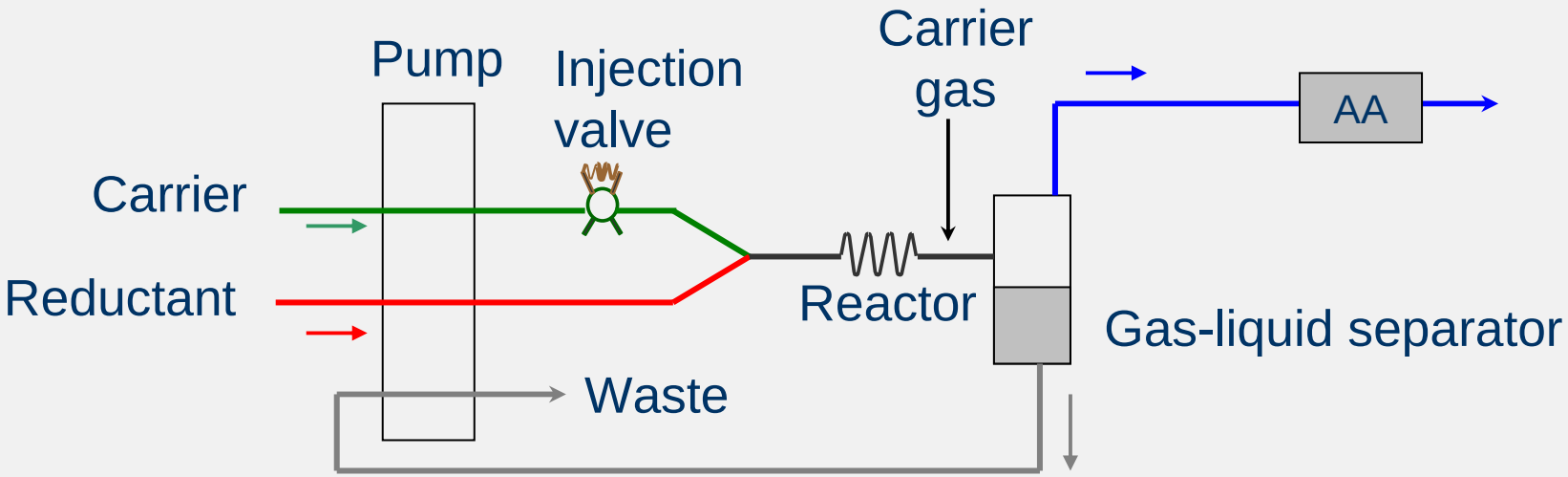
ICFIA 2005



- Batch systems
- Flow systems
  - Segmented flow analysis (SFA)
  - Continuous sample flow
  - Flow injection analysis (FIA)

    Andrade et al,1983, *Spectrochim. Acta*

CVAAS - Flow injection system (FIA)



- sampling rate
- small and variable sample volumes
- higher precision

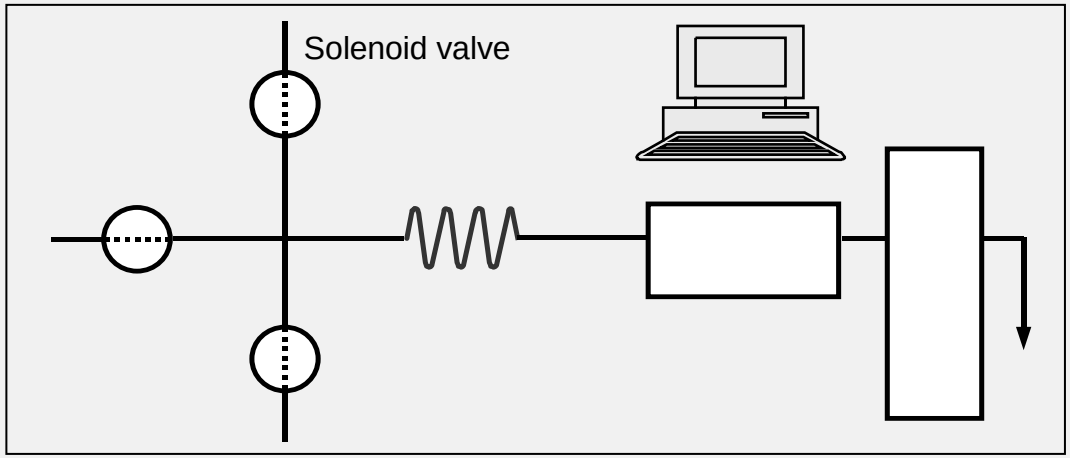
- Batch systems
- Flow systems
  - Segmented flow analysis (SFA)
  - Continuous sample flow
  - Flow injection analysis (FIA)

    Andrade et al,1983, *Spectrochim. Acta*
  - Sequential injection analysis (SIA)

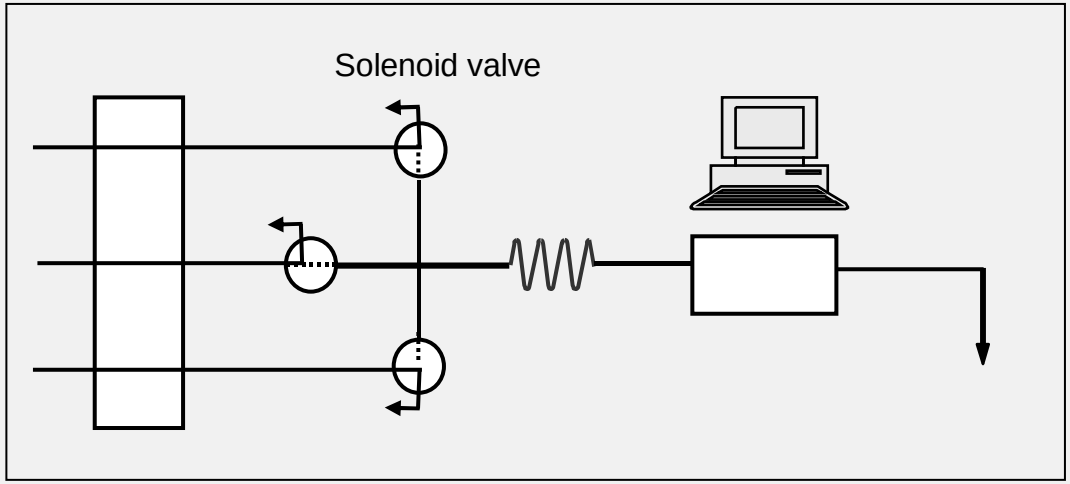
Multicommutation (MC)

Reis et al, ACA 293(1994)129.

Aspiration



Propulsion



Advantages

- Miniaturisation of flow systems
- Improved mixing conditions
- Reduced sample and reagent consumption
- Flexibility

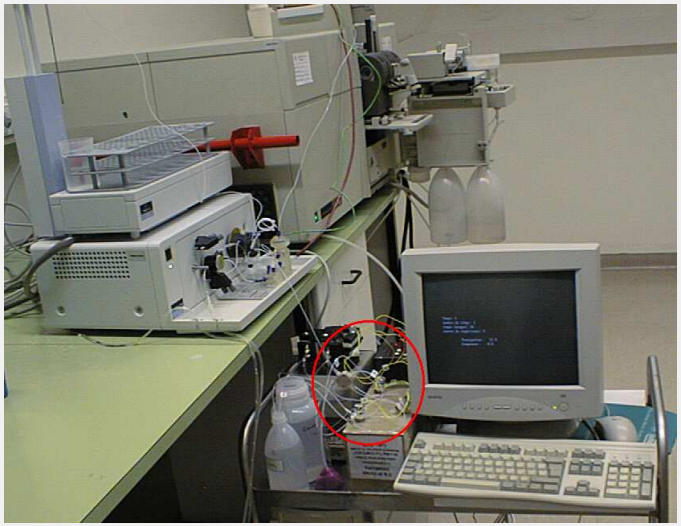
Limitations

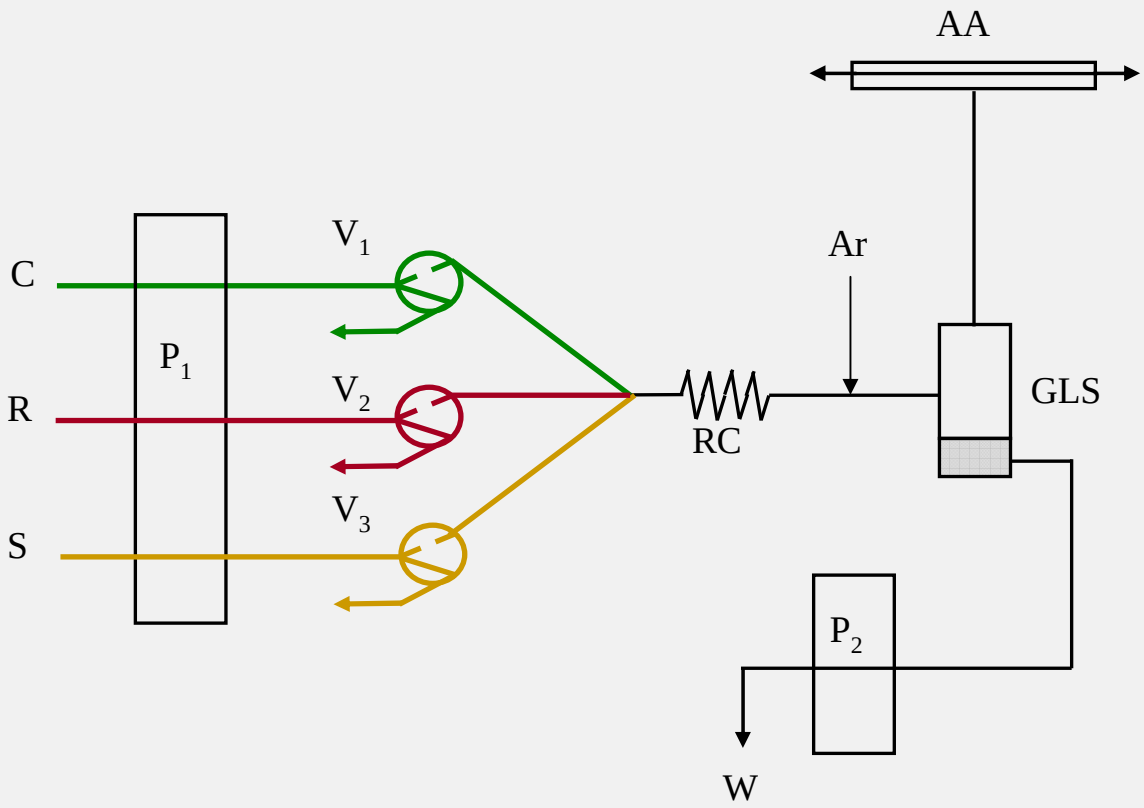
- The need to aspirate the solutions (or re-circulating the solutions)
- Limited commercial availability
- Lack of robustness of the valves

Objectives

- Calibration procedure using a single standard solution
- Reagent/sample reduction
- Waste reduction
- Application to the determination of mercury in fish samples

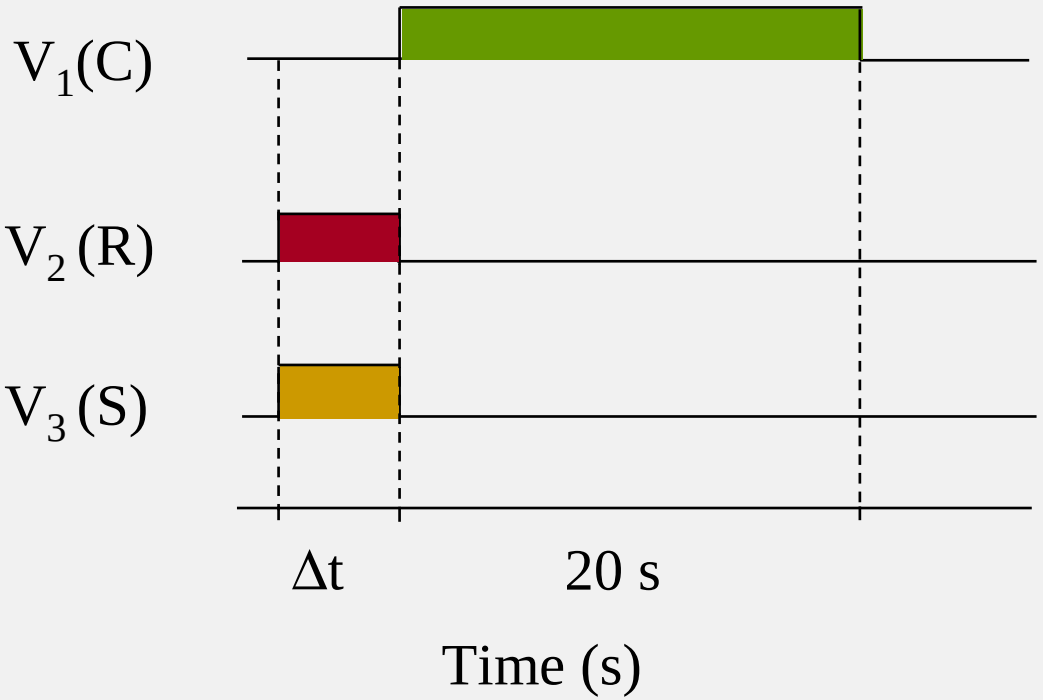
Flow manifold





C: carrier HCl 3% v/v (flow rate: 11 ml min^{-1}); **R**: reducing solution $NaBH_4$ 0.2% m/v in NaOH 0.05% m/v (flow rate: 6 ml min^{-1}); **S**: sample/standard solutions; **RC**: reactor, 30 cm; **Ar**: argon (flow rate: 70 ml min^{-1}); **AA**: atomic absorption spectrophotometer; **V_1-V_3**: solenoid valves; **GLS**: gas-liquid separator; **P_1,P_2** : peristaltic pumps; **W**: waste.

Timing course of the valves



Single standard calibration → **Δt: sampling time (0.5-10 s)**

Traditional calibration → **Δt: sampling time (5 s)**

Figures of merit

	FIAS 100	***MCFIA***	***MCFIA Single standard calibration (10ppb)***
Limit of detection (ng)	0.08	0.13	0.10
Limit of quantification (ng)	0.21	0.34	0.34
RSD %	4.7 (0.83 ng)	5.8 (0.83 ng)	6.2 (0.80 ng)
	1.7 (4.1 ng)	2.7 (4.2 ng)	1.9 (4.9 ng)
Linear range (ng)	0 – 10	0 – 10	0 – 10
Regression equation [b]			
m, slope	0.112 (±0.005)	0.130 (±0.008)	0.112 (±0.006)
b, intercept	0.014 (±0.014)	0.002 (±0.002)	0.018 (±0.012)
Correlation coefficient	0.9998	0.9994	0.9988
Sampling rate	90 h^{-1}	60 h^{-1}	60 h^{-1}

[b] Mean ± std deviation of 7 different working days

Figures of merit (cont)

	FIAS 100	MCFIA	MCFIA Single standard calibration (10 ppb)
Sample consumption [b]	500 µl	500 µl	50 – 1000 µl
HCl consumption [b]	0.25 ml	0.11 ml	0.11 ml
$NaBH_4$ consumption [b]	0.9 mg	1.0 mg	0.1 – 2.0 mg
NaOH consumption [b]	0.23 mg	0.25 mg	0.025 – 0.50 mg
Waste [b]	13.3 ml	4.7 ml	3.8 – 5.7 ml

[b] Values per assay

Accuracy

	Certified value mg/Kg	MCFIA [b] mg/Kg	MCFIA Single standard calibration [b] mg/Kg
Dogfish (DORM-2)	4.64 ± 0.26	4.37 ± 0.13	4.44 ± 0.28

[b] average value ± std deviation of two working days with 3 replicates analysed each day (n=6)

Accuracy

	Without spike (µg/Kg)	Spiked (ng)	MCFIA Recovery (%) [b]	MCFIA Single standard calibration Recovery (%) [b]
Cod	57	200	98.6 ± 0.8	104.6 ± 0.9
		500	99.8 ± 0.3	109.6 ± 0.4
		1000	96.9 ± 2.5	104.5 ± 2.6
Shellfish	≤ LOQ (9 µg/Kg)	200	90.7 ± 5.5	96.6 ± 3.7
		500	94.1 ± 2.7	105.6 ± 3.3
		1000	95.4 ± 1.2	107.1 ± 1.3

[b] Mean ± std deviation (n=3)

Slope comparasion method

Different volumes of the same sample/standard solution are intercalated in the system

⬇

plotting peak area versus injection time

⬇

sample calibration curve

The linear relationship $A = m\,V + b$

theoretically b=0

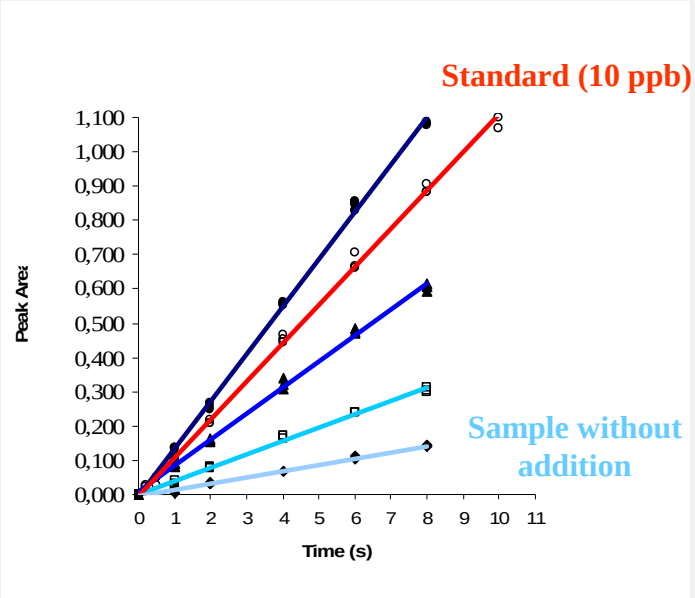
Beer's law $A = \varepsilon\, l\, C$

$$C^{*} = \frac{C_{std} \times m^{*}}{m_{std}}$$

Slope comparasion method

	Correlation coefficient	Slope [b]	Recovery [b] %
Sample without addition	0.9975	0.018±0.001	-
Sample solution			
Addition 2 ppb	0.9976	0.039±0.001	92.4±7.6
Addition 5 ppb	0.9995	0.076±0.001	103.6±3.7
Addition 10 ppb	0.9994	0.138±0.001	107.2±2.3
Standard 10 ppb	0.9995	0.111±0.002	-

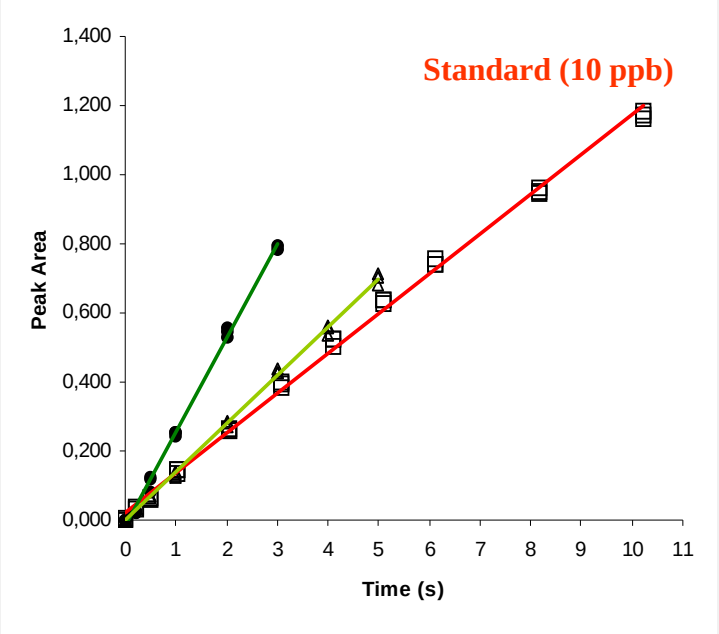
[b] mean ± Std deviation (n=3)



Slope comparasion method

	Correlation coefficient [b]	Slope [b]	Concentration Hg mg/Kg [b]
Dorm-2 (Dogfish)	0.9982	0.266±0.011	4.54±0.02
Dorm-2 Diluted solution	0.9996	0.140±0.003	4.77±0.09
Standard 10 ppb	0.9987	0.115±0.001	-

[b] Mean ± Std deviation (n=3)



Dogfish (Dorm-2): Certified value = 4.64± 0.26 mg/Kg

Making use of the linear relation between the signal (peak area) and injection time the concentration of the sample can also be accurately determined.

Conclusions

- ✓ The developed multicommutated flow system is accurate and precise for the determination of mercury in fish samples
- ✓ Advantage over the traditional calibration
  - Less time consuming
  - Reagent/standard consumption
  - Waste production
- ✓ Sample dilution is easily adjusted
- ✓ This methodology can be extended to other elements forming volatile hydrides

Acknowledgements

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