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DETERMINATION OF SELENIUM IN ENVIRONMENTAL SAMPLES USING A MULTICOMMUTED FLOW INJECTION SYSTEM WITH HGAAS

Fátima Silva, Ildikó V. Tóth, António O. S. S. Rangel

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Selenium

HGAAS - Principle

$$Se(IV) \xrightarrow[\text{Reductant } (BH_4^-)]{} SeH_2 \xrightarrow[\text{Carrier gas } (Ar;\ N_2)]{} \text{AAS } (\lambda = 196.0 \text{ nm})$$

HGAAS

- Holak W., Anal. Chem. 41 (1969)

Gas-Sampling Technique for Arsenic Determination by Atomic Absorption Spectrophotometry

Walter Holak
Food and Drug Administration, 850 Third Ave., Brooklyn, N. Y. 11232

IN CONVENTIONAL atomic absorption spectrophotometry a solution of the sample is introduced into the flame as an aerosol by means of a nebulizer. However, commercial nebulizers are only about 5% efficient in forming fine droplets suitable for atomization by the flame (*1*). Furthermore, a solution aspirated at a usual rate of 3–5 ml/min for about 10 sec produces a concentration signal extending over the length of aspiration. Theoretically, if the element were introduced into the flame rapidly—*e.g.*, 1 second—with no loss, a high narrow signal should result and the detection limit should improve.

Several devices aimed at improving the efficiency of atomic absorption sampling have been described in the literature. One scheme, developed by Brandenberger and Bader (*2*) was used to determine nanogram amounts of mercury. In their technique, mercury in solution was deposited on a copper wire and placed in the arm of a specially constructed cell with quartz windows. An electrical potential applied across the wire volatilized the mercury instantaneously. The mercury vapors were then swept through the cell with air and the atomic

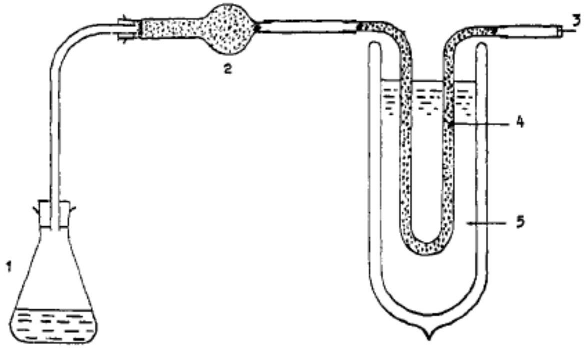


Figure 1. Arsine generator and liquid nitrogen trap

1. Arsine generator
2. Calcium chloride
3. Needle
4. Glass beads
5. Liquid nitrogen

FIA - HGAAS

- O. Åström, Anal. Chem. 54 (1982)

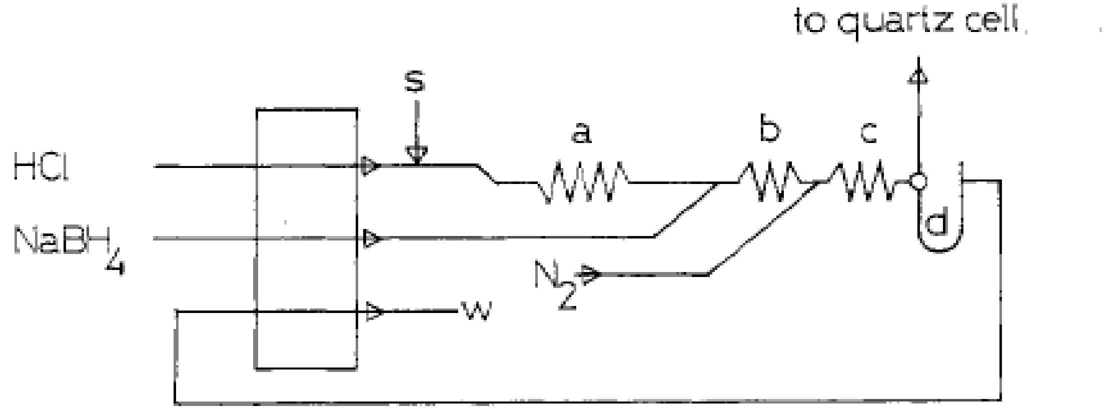


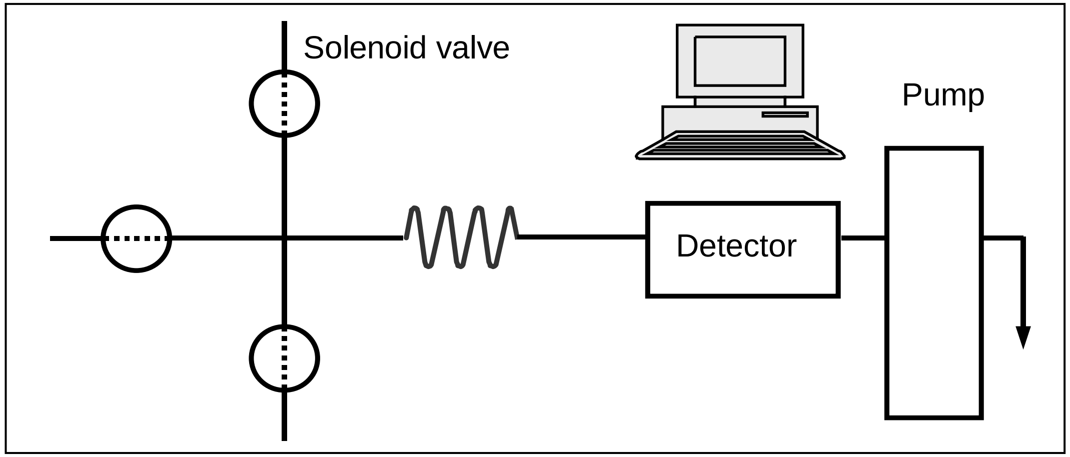
Figure 1. Flow injection manifold for determination of bismuth with the atomic absorption hydride technique: (s) point of injection (sample loop); (a), (b), and (c) coils, i.d. 0.7, 0.5, and 0.5 mm, respectively; (d) gas–liquid separator; (w) waste. (For flow rates and coil length see text.) Sodium borohydride is 1% in 0.1 M NaOH and hydrochloric acid 1.2 M in all figures if not stated otherwise.

Multicommutation (MC)

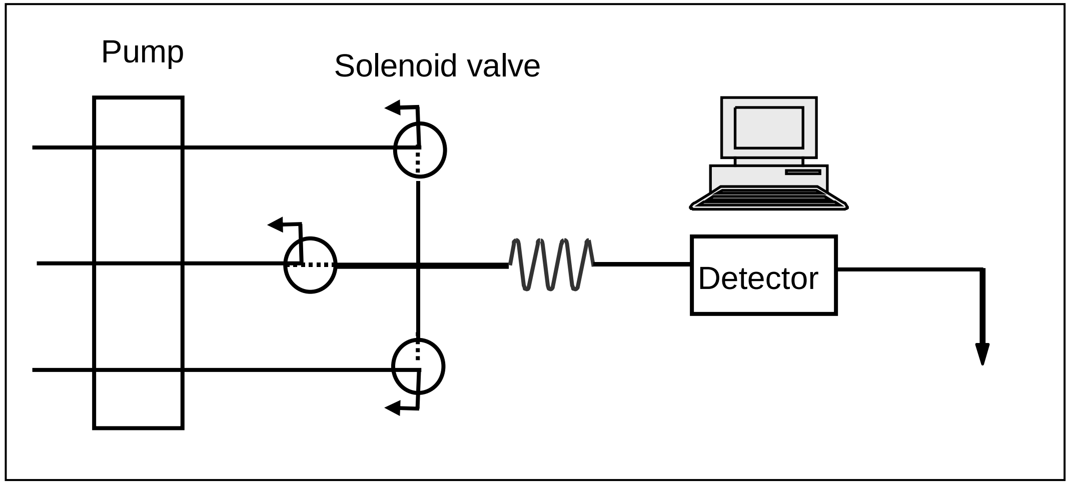
Reis et al, ACA 293(1994)129.

Multicommutation (MC)

Aspiration



Propulsion



Multicommutation

Advantages

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

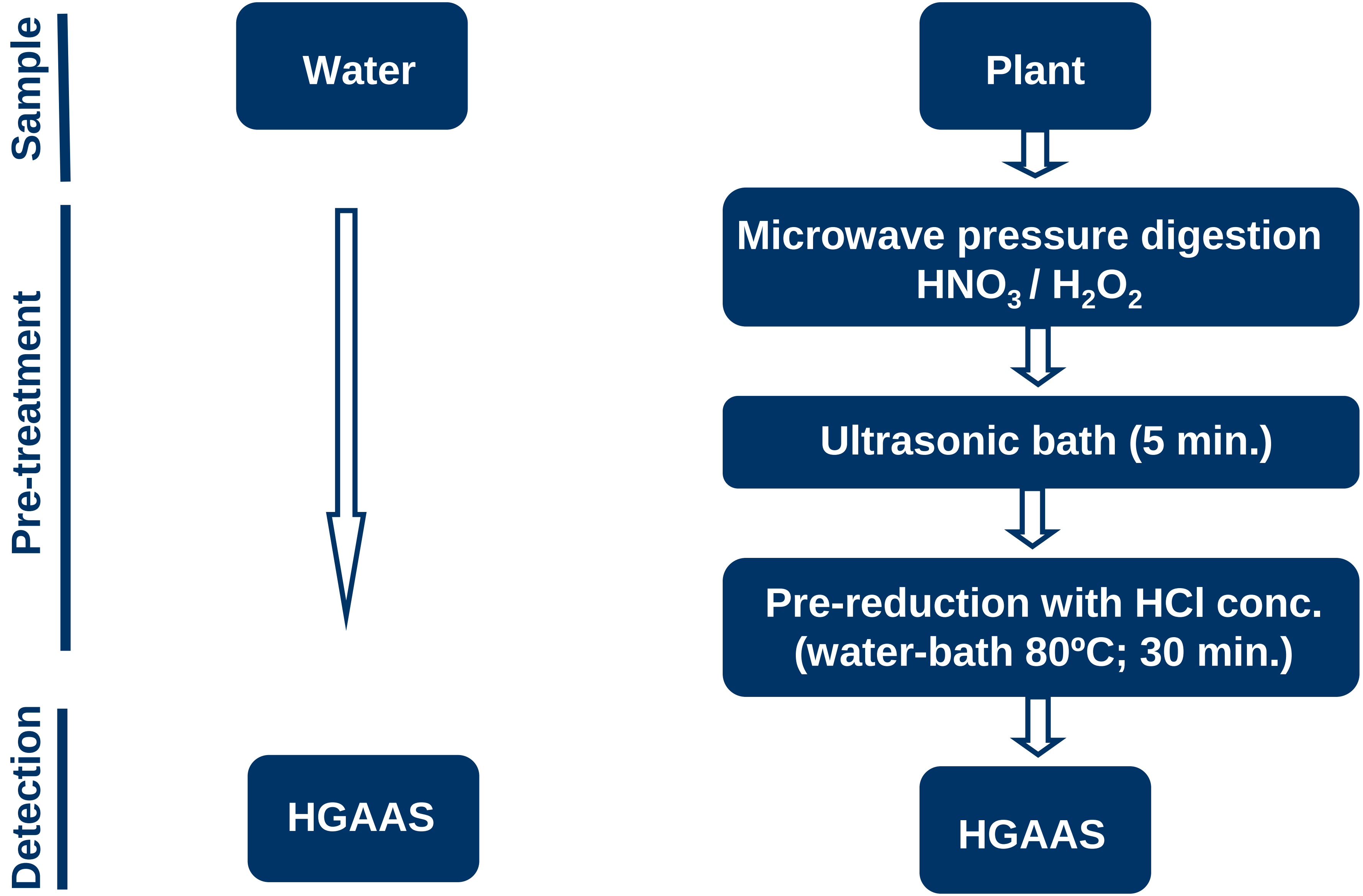
Limitations

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

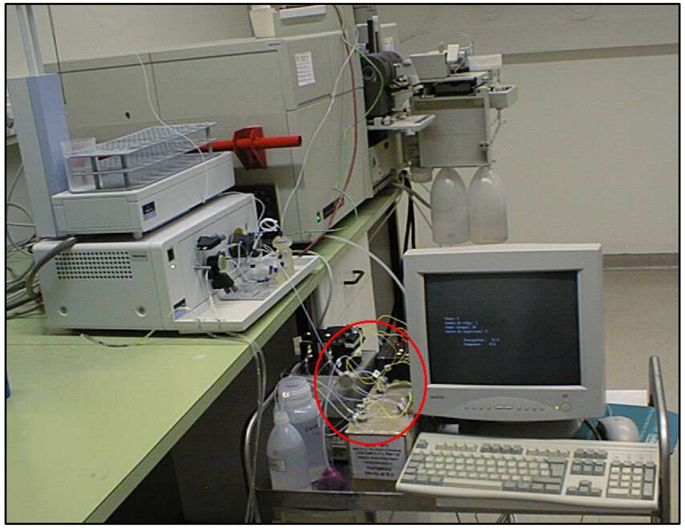
Objectives

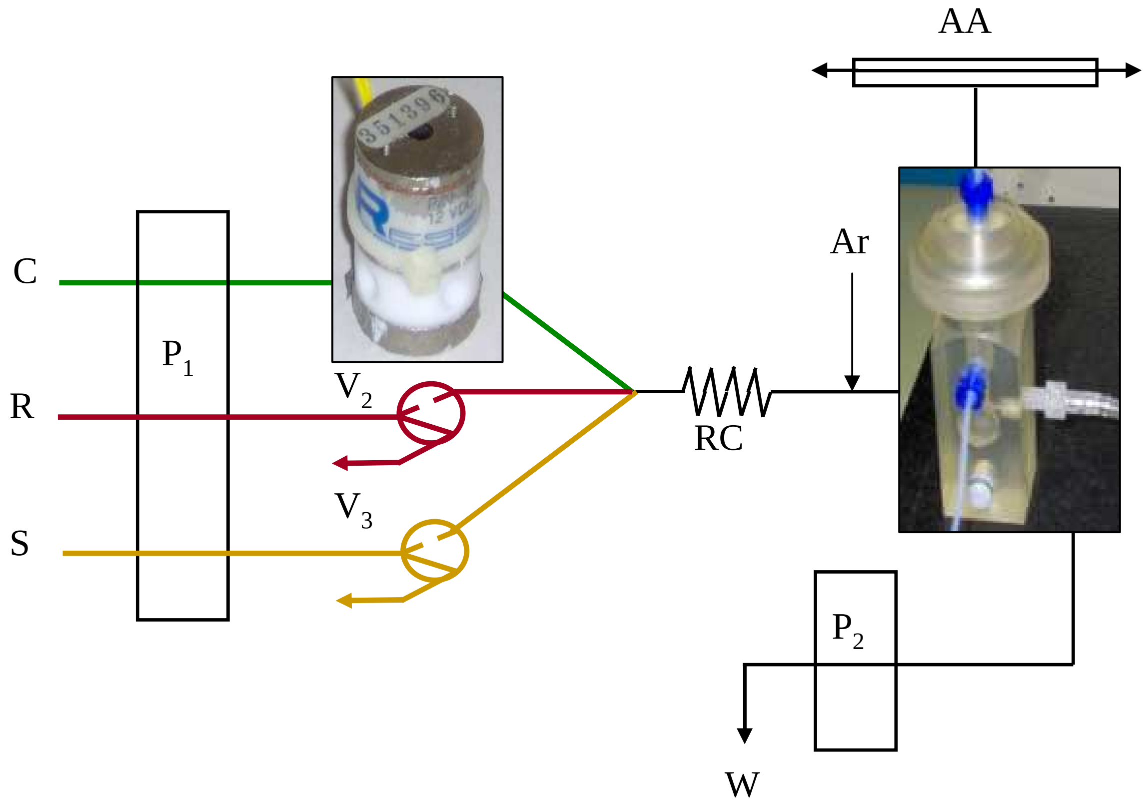
- Reagent/sample reduction
- Waste reduction
- Application to the determination of environmental samples

Sample treatment



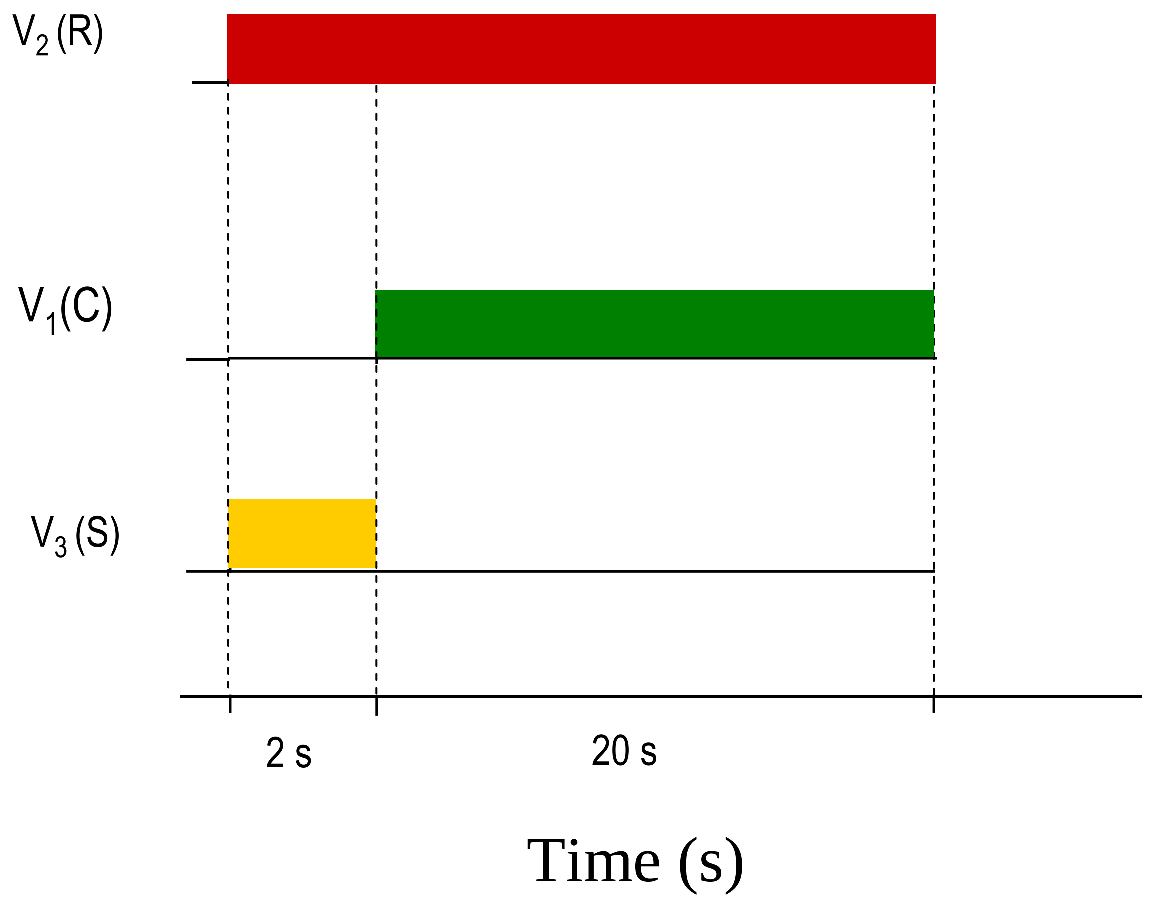
Flow manifold





C: carrier HCl 10% 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, 100 cm; **Ar**: argon (flow rate: 100 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



Figures of merit

	MCFIA	FIAS
Limit of detection (3σ) / μg l^{-1} (n=10)	0.8	0.2
Limit of quantification (10σ) / μg l^{-1} (n=10)	1.5	0.5
RSD %	2.9 (2.5 μg l^{-1})	2.7 (2.5 μg l^{-1})
	3.0 (10 μg l^{-1})	1.3 (10 μg l^{-1})
Dynamic working range / μg l^{-1}	1.5 – 10	0.5 – 10
Regression equation [b]		
m, slope / μg l^{-1}	0.0236 (±0.0030)	0.0574 (±0.0092)
b, intercept	0.0059 (±0.0048)	0.0098 (±0.0081)
Correlation coefficient	0.9992	0.9996
Determination rate / h^{-1}	116	116

[b] Mean ± std deviation of 5 different working days

Figures of merit (cont)

	MCFIA	*FIAS*
Sample consumption [b]	210 µl	500 µl
Reagent consumption [b]		
HCl	0.4 ml	0.6 ml
$NaBH_4$	4.4 mg	6.2 mg
NaOH	1.1 mg	1.6 mg
Waste [b]	6.4 ml	9.3 ml

[b] Values per assay

Accuracy

Reference Material	*Certified Value* [a]	*MCFIA* [b]	*Number of replicates*
Sea Lettuce (CRM 279)	593 ± 32 μg kg^{-1}	530 ± 16 μg kg^{-1}	5
Surface Water (SPS-SW2)	10.0 ± 0.05 μg l^{-1}	10.2 ± 0.3 μg l^{-1}	3
Tr-218 (Inter 2000)	2.5 ± 2 μg l^{-1} [c]	2.7 ± 0.1 μg l^{-1}	15

[a] Certified value ± uncertainty
[b] Average value ± std deviation of the results
[c] Proficiency testing mean ± half with of the acceptance interval

Conclusions

The developed multicommuted flow system has proved to be rapid and accurate for the determination of selenium in environmental samples.

- ⇓ Reagent/standard consumption
- ⇓ Waste production

This methodology can be extended to other elements forming volatile hydrides.

Acknowledgements

Porto – Portugal

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