Spectrophotometric assay in a MSFIA system using a liquid waveguide capillary cell: application to zinc and copper determination in natural waters

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Introduction

Zinc and copper ions are essential for normal physiological processes of living organisms. Both are involved in various biochemical processes and are essential for the functioning of some enzymes. Therefore, it is crucial to develop simple, robust and low cost methods to accurately determine their concentration in water samples.

Most of flow analysis systems for the determination of zinc and copper use spectrophotometric detection (simple, fast, robust). In natural waters, they are present at very low concentrations and to avoid the use of a more complex experimental set-up, a liquid waveguide capillary cell (1.0 m pathlength, 550 μm i.d. and 250 μL internal volume) was applied to increase the sensitivity of the spectrophotometric detection mode. The determination of zinc and copper is based on the colorimetric reaction with zincon at different pH values. For flow manipulation/programming a multi-syringe flow injection analysis (MSFIA) was applied.

The detection limits for copper and zinc were 0.1 and 2 μg L^{-1}, respectively. The system provided a linear response up to 100 μg L^{-1} with a throughput of 43 h^{-1}, and low reagents consumption and effluent production. The developed work was applied to natural waters and the accuracy was assessed using three certified reference water samples.
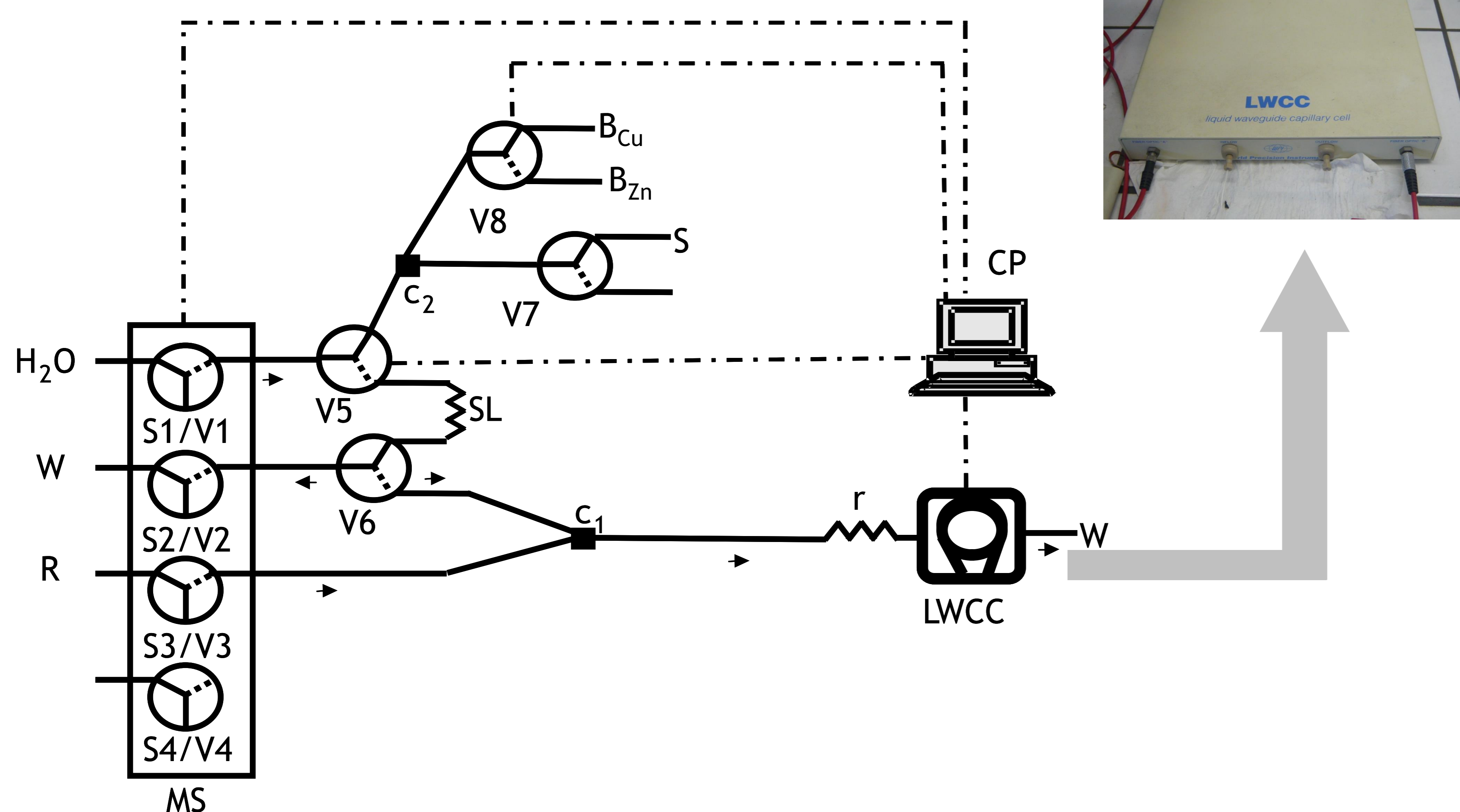
Manifold

Figure 1. Multi-syringe flow injection analysis manifold for the determination of zinc and copper in waters. Si: syringes, Vi: solenoid valves; SL: sample loop (400 μL); r: reaction coil (200 cm); ci: confluences; LWCC: detector (100 cm of optical path); CP: computer; W: waste; S: sample or standard; B_{Cu}: Copper buffer solution; B_{Zn}: Zinc buffer solution; R: color reagent (zincon, 620 nm).

Protocol sequence

Step	Piston movement	Position of syringes and solenoid valves							Volume (mL)	Flow rate (mL/min)	Description
		S1	S2	S3	V5	V6	V7	V8			
1	Pick up	0	1	0	1	1	1	1^a/0^b	1.4	5	Aspirate sample and buffer solution
2	Dispense	1	0	1	0	0	0	0	0.5 C 0.25 R	1.5 C 0.75 R	Propel carrier and color reagent to the detector
3	Dispense	1	0	0	0	0	0	0	2.0	4	Propel the mixture to the detecor and signal registration

Note: 0 - off; 1 - on; The volume and the flow rate are presented with respect to syringe 1. Syringe 1 and 2 have 5 mL of capacity and syringe 3 and 4 have 2.5 mL of capacity; C - carrier; R - color reagent; a - copper buffer solution; b - zinc buffer solution;

Interference studies

Specie tested	Copper		Zinc	
	Concentration (μg L^{-1})	Relative deviation (%)	Concentration (μg L^{-1})	Relative deviation (%)
Iron	40	+5.3	200	+3.6
Aluminium	2000	-4.9	200	+4.9
Cadmiun	20000	+4.8	40	+5.1
Manganese	200	+4.8	20	+3.3
Lead	20000	+5.1	1000	+5.4

* using a standard solution of 20 μg L^{-1} of copper or zinc

Figures of merit

	Copper	Zinc
Detection limit (ppb) *	0.1	2
Quantification limit (ppb)	0.8	4
Working range (ppb)	Up to 100	Up to 100
Determination rate (h^{-1})	43	43
Reagent consumption (μmol/assay)		
Zincon	0.01	0.01
Sodium hydroxide	---	35
Potassium chloride	---	7
Boric acid	---	18
Sodium acetate	140	---
Waste produced (mL/assay)	3.75	3.75

* - assessed from three times the standard deviation from blank signal (n=10)

Application to water samples

Analyte	Sample number	Recovery (%)		
		Concentration added		
		4 μg L^{-1}	10 μg L^{-1}	20 μg L^{-1}
Zinc	1	102 ± 6	96 ± 4	103 ± 6
	2	96 ± 6	93 ± 2	104 ± 6
	3	94 ± 7	107 ± 9	104 ± 3
	4	104 ± 4	107 ± 5	105 ± 1
Copper	1	97 ± 2	100 ± 2	102 ± 1
	2	102 ± 1	102 ± 1	103 ± 1
	3	102 ± 3	99 ± 1	104 ± 1
	4	99 ± 5	95 ± 3	94 ± 1

1 - Well water; 2 - Spring water; 3 - Groundwater; 4 - Seawater; n=5;

Certified water samples

Sample	Copper (μg L^{-1})		Zinc (μg L^{-1})	
	MSFIA-LWCC	Certifed value[d]	MSFIA-LWCC	Certifed value[d]
ERM-CA021a	2028 ±50[a]	1975 ±54	669 ±231[a]	514 ±9[a]
NIST-SRM 1640	87 ±2[b]	85.2 ±1.2	67 ±6[b]	53.2 ±1.1
NWRI-TM-24.2	8.2 ±0.2[c]	7.3 ±0.1	22.8 ±2.8[c]	20 ±0.5

[a] standard deviation (n=20), dilution 50 times; [b] standard deviation (n=10), dilution 5 times; [c] standard deviation (n=10), no dilution; [d] mean and associated uncertainty