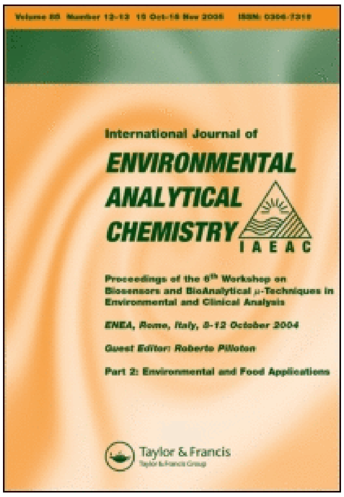

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Tubular potentiometric detector used to determine As(V) in sediment extracts by flow injection

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The construction and evaluation of a tubular potentiometric detector sensitive to As(V) ions is described. This electrode, with no inner reference solution, is comprised of a FeOOH–SiO_2–graphite composite agglutinated with an epoxy resin. For As(V) ion concentrations in the range 1.0×10^{-5} to 1.0×10^{-1} mol L^{-1}, the sensor is used as the selective electrode in an FIA system along with a commercial Ag/AgCl reference electrode. In optimal conditions, the practical limit of detection is 4×10^{-6} mol L^{-1} and a sampling rate of 40 h^{-1} can be achieved. The system was applied to estimate As(V) levels in sediments of a drinking water distributor in Zimapán (Mexico), an area known to be polluted with this element. The As(V) concentrations detected in the different extracts of sediments generated by the sequential modified BCR three-step extraction procedure (BCR-SEP) were comparable to those obtained by electrothermal atomic absorption spectroscopy (ET-AAS).

Keywords: Arsenic; Tubular detector; Flow injection analysis; Sequential extraction

1. Introduction

In the environment, arsenic (As) is released from rocks through natural processes (erosion, leaching) but may also find its way into the environment when it is used, for example, in pesticides, wood preservatives, in the manufacture of glass, electronic parts or drugs, or as a residue of low-grade carbon [1, 2]. In non-polluted soils, the levels of As are usually in the range 0.2–40 mg kg^{-1}. However, there are cases in which the generalised use of arsenic pesticides has led to As concentrations in agricultural soils as high as 200–2500 mg kg^{-1}. These levels are comparable to those found in areas around copper smelting furnaces [3, 4].

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The most generally applied methods of As detection are inductively coupled plasma (ICP) spectroscopy, ion chromatography (HPLC), electrothermal atomic absorption spectroscopy (ET-AAS) or hydride generation AAS (HG-AAS) [5–8], and voltametry [9]. Potentiometric methods are only occasionally used, for instance, to detect titration end points for high As concentrations [10], although their use in water by coupling to preconcentration systems based on iron oxyhydroxides embedded in silica gel has recently been reported [11]. Notwithstanding, potentiometric detectors have the advantage of being sensitive over a wide concentration range and the use of a tubular electrode in flow injection analysis avoids altering the hydrodynamic conditions of the system [12–15].

The aim of the present study was to design, construct and evaluate a tubular electrode without an internal reference solution selective to As(V) ions, based on a FeOOH–SiO_2–graphite membrane agglutinated with an epoxy resin. The response of this electrode is the result of the selective adsorption of As(V) ions onto the active component of the membrane, most likely as $[FeO(AsO_4)]^{2-}$ [16]. The electrode is therefore selective for these species based on an ion exchange mechanism and not on redox phenomena.

The procedure for determining the arsenate ion was optimised using several chemometric techniques: the two-level complete factorial design followed by the supermodified simplex method [17]. In the optimal conditions proposed, we then determined As(V) in the different sludge extracts of the water distributor in Zimapán (Mexico) generated by the modified BCR three-step sequential extraction procedure (BCR-SEP) [18]. These results were then compared to those obtained through ET-AAS.

The area selected for our study was the hydrological basin of the river Lerma found in the hydrological subbasin of the river Moctezuma, which flows into the Gulf of Mexico. The area is a mining region producing lead, zinc, copper, iron, gold and silver. The industrial exploitation of its natural resources may have contributed in some measure to the deterioration of the hydrogeologic system of this region, and its groundwater has a high level of As content. A possible source of contamination could be sediments in the distributor system. Thus, the degree of As leaching from these sediments should be examined according to the aggressiveness of the reagent used.

2. Experimental

2.1 *Constructing the tubular electrode*

The active component of the sensor is iron oxi-hydroxide embedded in silica gel. For its preparation, 4.1013 g of $FeSO_4 \cdot 7H_2O$ (Baker, precursor of FeOOH) dissolved in 22.0 mL of distilled water are transferred to a flask containing 20.0 mL of tetraethoxysilane (TEOS, Panreac 98%) and 17.0 mL of ethanol (at a $[TEOS]/[Fe^{2+}]$ molar ratio of 5). Condensation of the alcoxide and ferrous ion precipitation are achieved by adding NH_3 in sufficient quantity to give a $pH = 10$. The ferrous ion oxidises to produce the ferric ion by bubbling air through the solution for 1 h at 60°C. The gel is then filtered, washed with deionised water and dried at 100°C for 24 h [see Ref. 19 for more details].

The detector membrane was prepared by mixing 0.0050 g of the active compound with 0.2450 g of ultrapure graphite powder (particle size 200 mesh supplied by Carbone Lorraine), 0.4200 g of epoxy resin (Araldite M, Ciba-Geigi) and 0.0800 g of

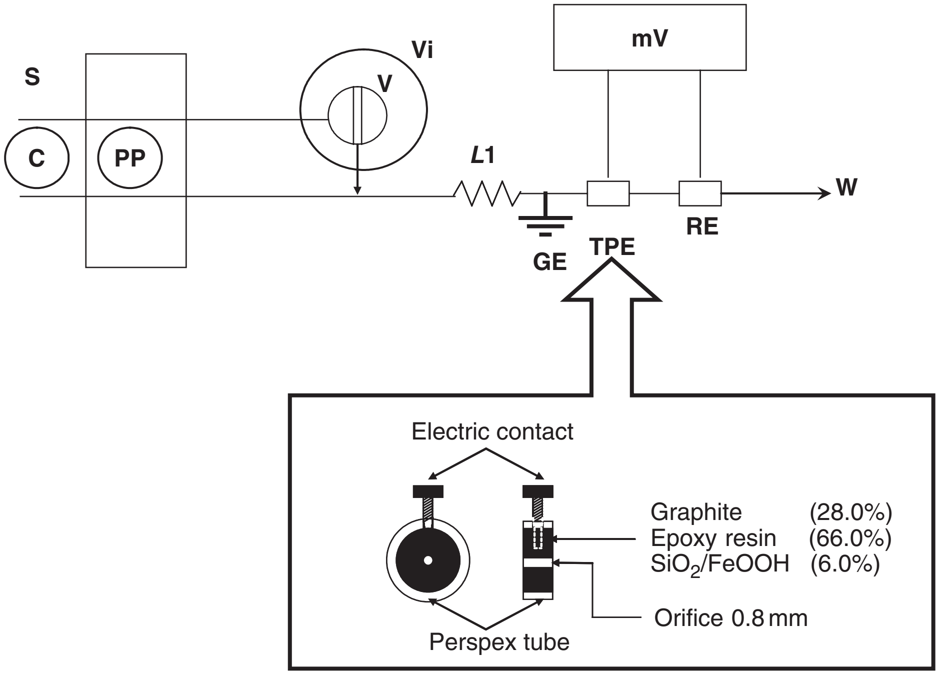

Figure 1. Diagram showing the manifold and the tubular electrode. Factors that may be affected are marked with a circle. S = sample, C = carrier, PP = peristaltic pump, V = injection valve, Vi = injection volume, *L*1 = reaction coil length, mV = milli-voltimeter, TPE = tubular potentiometric electrode, RE = reference electrode, G = ground, W = waste.

Araldite HR as hardener. The mixture was transferred to a Perspex tube (5 mm length and 7 mm inner diameter) into which was inserted the internal conductor of the shielded electric cable. After drying (50°C, 24 h), a tubular channel of 0.8 mm inner diameter was drilled through the central core of the electrode (figure 1). The electrode is polished by introducing a cotton thread impregnated with alumina powder (BDH 3 µm) through the orifice and rubbing adequately. The electrode was polished daily even when there was no apparent decrease in the slope or delayed response time.

As reference electrode, we used an Orion model 90-02-00 double junction silver/silver chloride in saturated KCl solution electrode with the external chamber filled with KNO_3 1 M solution.

2.2 *Flow injection manifold*

Solutions were propelled by a four-channel Gilson Miniplus 2 peristaltic pump fitted with propulsion tubes of the same brand. The sample to be analysed was injected into the carrier flow using a Rheodyne ref.50 four-way rotary valve. The different components of the FIA manifold were connected using Omnifit Teflon tubing (0.8 mm internal diameter) and Gilson connectors. Confluences, reference electrode supports, the ground electrode and other parts used in this manifold were homemade as previously reported [20]. Potentials were measured using an Autolab instrument (Echo Chemie, Utrecht, Netherlands) equipped with a PGSTAT 10 controlled by GPES software v. 4.6 (Echo Chemie).

2.3 *Evaluation of the tubular electrode*

The characteristics of the response shown by the tubular potentiometric detector were determined in a manifold as shown in figure 1. Carrier composition was optimised using the supermodified simplex procedure varying the phosphate concentration from 0.1 to 1.0 $\mathrm{mol\,L^{-1}}$ and the pH from 4 to 9. In addition, EDTA was added to the carrier to avoid undesirable effects due to Ca precipitation in samples.

Selectivity coefficients were determined by the two-solution method [21] using interfering ion concentrations of 1×10^{-3} and $1 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$ As(V).

2.4 *Preparation of sediment extracts*

Sediments from the drinking water distributor of Zimapán, Hidalgo (Mexico) were analysed according to the BCR scheme [18] by sequentially exposing solids to: (a) acid conditions – 0.5 g of sample were treated with 20.0 mL of a 0.11 $\mathrm{mol\,L^{-1}}$ acetic acid solution and centrifuged for 5 min at 5000 rpm (extract 1); (b) reducing conditions – 20.0 mL of a 0.1 $\mathrm{mol\,L^{-1}}$ hydroxylamine chloride solution (adjusted to pH ~ 1.5 using 2 $\mathrm{mol\,L^{-1}}$ HNO_3) were added to the residue from the first extraction and centrifuged (extract 2); and (c) oxidizing conditions – the residue from the second extraction was treated with 5.0 mL of 8.8 $\mathrm{mol\,L^{-1}}$ H_2O_2 (adjusted to pH 2–3 using 2.0 $\mathrm{mol\,L^{-1}}$ HNO_3) (extract 3). In parallel, 0.5 g of the sediment sample was completely mineralised by treatment with 5.0 mL of concentrated nitric acid and 5.0 mL of perchloric acid and drying in a sand bath. The residue was extracted with deionised water and made up to 100.0 mL in a volumetric flask. Residual metals were determined as the difference between the amounts obtained through complete mineralisation and the sum of those obtained in the three sequential extractions.

3. Results and discussion

3.1 *Evaluation of the flow system*

To evaluate the behaviour of the system, we used the slope value of the calibration plot obtained for As(V) concentrations in the range 1×10^{-4} to $1 \times 10^{-1}\,\mathrm{mol\,L^{-1}}$. Optimal values established for the carrier were 0.5 M $H_2PO_4^-/HPO_4^{2-}$ (1 : 1 molar ratio) and pH = 7. As(V) at a concentration of $1 \times 10^{-6}\,\mathrm{mol\,L^{-1}}$ was added to establish the baseline.

Figure 1 shows that the factors affecting the response were: the concentration of EDTA in the carrier (because of the high calcium content of the sludge), the flow rate (F), the injection volume (Vi) and the reactor length ($L1$). The length of the reactor $L1$ was fixed at 60 cm since the results of several trials indicate that a shorter length reduces signal reproducibility, reduced signals being observed at lengths above 60 cm due to increased sample dispersion.

Two levels of the remaining factors were selected (see table 1) for a complete factorial design (replicates, i.e., 2^{3+1}) allowing us to identify which factors were critical. Sixteen experiments were performed in random order. The design matrix and values obtained

Table 1. Selected levels of each factor.

	Level	
Factor	−1	+1
[EDTA] (*M*) (mol L^{-1})	0.0	0.01
Flow rate (*F*) (mL min^{-1})	0.1	3.0
Injection volume (Vi) (μL)	20.0	100.0

Table 2. Matrix design and experimental results.

M	F	Vi	Slope (mV $decade^{-1}$)		Mean (mV $decade^{-1}$)
−1	−1	−1	6.07	6.68	6.38
+1	−1	−1	12.92	13.40	13.16
−1	+1	−1	8.42	7.44	7.93
−1	−1	+1	14.25	15.90	15.07
−1	+1	+1	15.24	12.04	13.64
+1	−1	+1	20.80	18.25	19.52
+1	+1	−1	16.59	19.34	17.96
+1	+1	+1	20.83	20.53	20.68

Table 3. *F*-factors and *p* values obtained in the factorial design used to optimise the FIA conditions for arsenate ion determination.

Factor	Main factor	Variance	F	*p*
M	24.162	200.3	53.88	0.0001
F	2.311	9.25	5.15	0.0530
Vi	64.517	137.9	143.87	0.0001
M–F	0.493	8.5	1.10	0.3250
M–Vi	1.772	7.08	3.95	0.0820
F–Vi	0.254	11.0	0.57	0.4730
M–F–Vi	0.027	0.110	0.06	0.8110

Factors in bold were found to be statistically significant in an ANOVA of the results ($F > 5.32$ and $p < 0.05$ at the 95% confidence level).

for the slope of the calibration line are provided in table 2. Suitable treatment of these data revealed the mean effect exerted by each factor on the standard curve (table 3, column 1). In turn, these values enabled us to calculate the variance of each factor using the Yates algorithm (column 3) [16]. By comparing the variance shown by each factor with the variance of the residuals (1.794), a Fischer *F*-test was then performed for each source of variation. These tests indicated that at a significance level of $p = 0.05$, the critical factors were the injection volume and the EDTA concentration in the carrier. We therefore went on to optimise the levels of these two factors, setting the flow velocity at 3.0 mL min^{-1} in an effort to achieve a rapid time of analysis.

3.2 *Optimisation of the analytical methodology*

The most appropriate value for the slope of the calibration line is the theoretical value of 30.0 mV $decade^{-1}$, such that this value was set as the optimisation target [16].

We performed a series of calibrations using standard As(V) solutions in the concentration range 1×10^{-4} to $1 \times 10^{-1}\,\mathrm{mol\,L^{-1}}$, modifying the carrier EDTA concentration and injection volume according to the criteria of the supermodified simplex (SMS) method [17]. Figure 2(A) shows the points selected and the changes in the simplex, whilst figure 2(B) shows the slope value obtained at each experimental point. After 10 experiments, the desired slope was obtained for a carrier EDTA concentration of $0.016\,\mathrm{mol\,L^{-1}}$ and an injection volume of 50 μL (Experiment 5 in figure 2B).

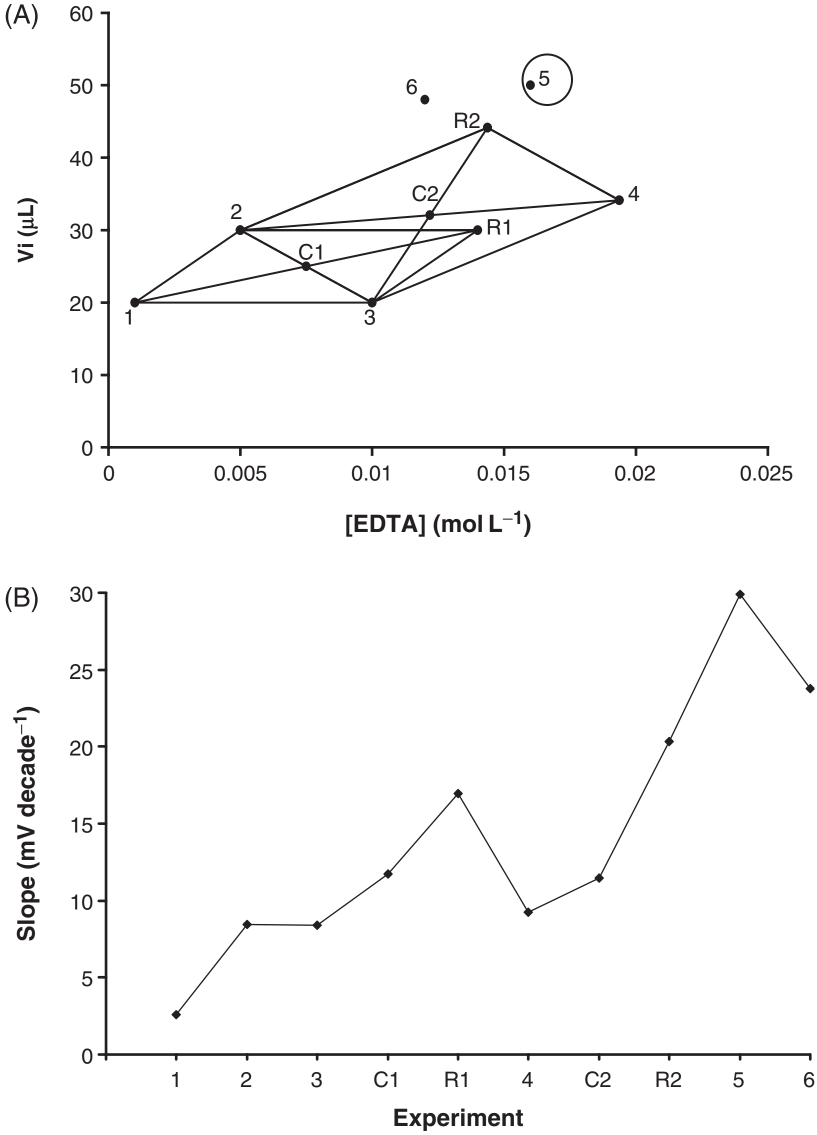

Figure 2. Changes in the slope of the standard curve produced in experiments performed during supermodified simplex optimisation of the injection variables.

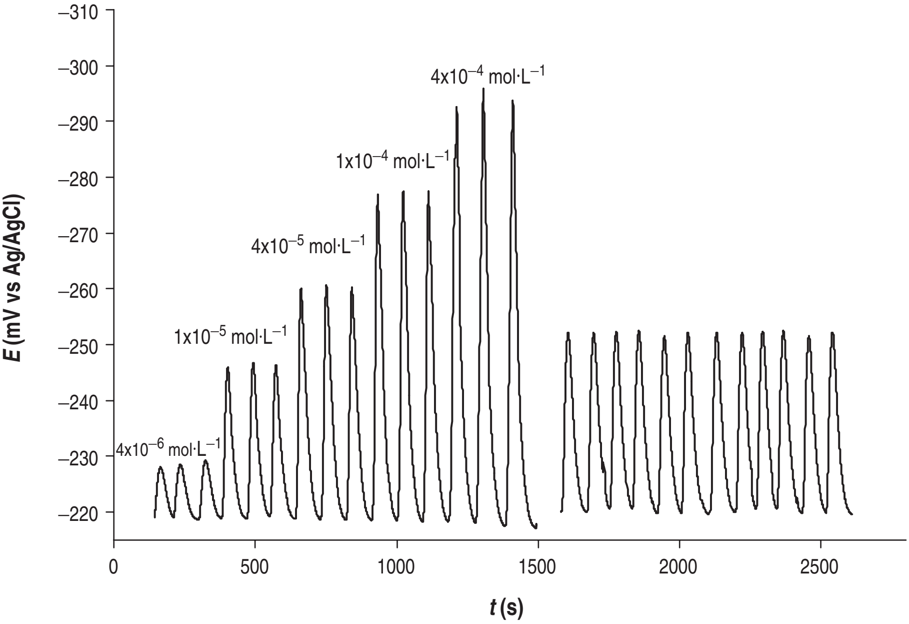

Figure 3. Recorder output of the tubular As(V) detector obtained for a calibration plot (between 4×10^{-6} and $4 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$) and for twelve successive injections of a 2×10^{-5} M solution of As.

Table 4. Characteristics of the tubular arsenate ion detector used in optimal conditions.

Parameter	Value and standard deviation
S ($\mathrm{mV\,decade^{-1}}$)[a]	−29.74 (0.7)
Const ($n = 6$)[a]	−324.9 (0.5)
Regression coefficient[a]	0.9970 (0.20)
Lineal range ($\mathrm{mol\,L^{-1}}$)[b]	1×10^{-1}–1×10^{-5}
LLLR ($\mathrm{mol\,L^{-1}}$)[b]	4×10^{-6}

[a] Values obtained in 6 replicate experiments. % RSDs appear in parentheses. S, slope; Const, constant of the modified Nerst equation. Results are expressed with respect to Ag/AgCl.

[b] Values obtained for a solution of ionic strength adjusted to 0.5 M ($H_2PO_4^-/HPO_4^{2-}$); LLLR, lower limit of the linear response.

From the FIAgram corresponding to these conditions (figure 3), we obtained the parameters of electrode quality shown in table 4. These values indicate that the reproducibility of the analytical signal generated by the tubular sensor is good, given the small relative standard deviation of the slope (0.7 %). Repeatability, determined for 12 injections of a given As(V) solution ($2 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$) (see figure 3) was 0.1% relative standard deviation. In these conditions it is possible to determine 40 samples per hour.

3.3 *Interferences*

Interference by other anions was evaluated by the two-solution method [21] using a concentration of the interfering ion of $1 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$. Anions such as chloride,

Table 5. Values of the selectivity coefficients for several ions, determined by the two solutions method with $1 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$ of interfering and $1 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$ of As(V).

Interfering ion	$\log K$
AsO_3^{3-}	−2.3
HPO_4^{2-}	−2.3
HCO_3^-	−2.1
NO_3^-	−3.1
CrO_4^{2-}	−2.6
I^-	−2.4
I_3^-	−2.7
Cl^-	−1.8

nitrate, acetate, phosphate and hydrocarbonate were selected because of their presence in the water and sediment extracts. Tri-iodine, iodine, chromate and arsenite were tested because of their redox properties. The selectivity coefficients calculated (as $\log K$) ranged from −1.7 for chloride to −2.9 for nitrate (see table 5), thus indicating the high selectivity of this electrode towards As(V).

3.4 *Analytical application*

Using the optimal conditions predicted by the SMS method, we determined As(V) levels in sediment samples taken from the drinking water distributor (table 4). Samples were obtained from two distributor points (right and left sides) every 6 months (1st semester, 2nd semester). The As(V) concentrations determined ranged from 63 to $126\,\mathrm{mg\,kg^{-1}}$. These levels are higher than concentrations found in unpolluted soils [3, 4]. Moreover, a paired *t*-test revealed no significant differences between the values determined using the proposed potentiometric system and those established by ET-AAS (table 6), indicating that in these samples practically all the As(V) occurs as arsenate. The results shown in table 6 suggest that As(V) is extracted mostly in stage 2, when the sample is treated with hydroxylamine in an acid medium. This suggests As(V) is essentially bound to iron and manganese oxides, which would be expected if we consider the affinity of the arsenate ions retained in the iron oxi-hydroxides present in solid samples [22]. This indeed forms the basis of the sensor developed.

4. Conclusions

Herein we describe a tubular electrode developed using a new material prepared by our team, which is selective towards As(V) ions in the concentration range 1.0×10^{-5} to $1.0 \times 10^{-1}\,\mathrm{mol\,L^{-1}}$. When incorporated in a flow injection system, the detector is capable of processing 40 samples per hour. This simple, low-cost system was successfully applied to the analysis of sediment extracts from a drinking water distributor operating in a region of soils polluted with mine tailings. The results generated are comparable to those obtained by ET-AAS, with the added advantages of speed, simplicity, low cost, easy transport for fieldwork etc. Our findings indicate that the As(V) in sediment extracts is mainly bound to iron and manganese oxides and, given

Table 6. As(V) determined in sediment extracts using the tubular sensor under the optimum conditions compared to those obtained by ET-AAS.

		$[AsO_4^{3-}]$ ($mg\,kg^{-1}$)				
Sample	Extraction	Tubular sensor	% RSD[a]	ET-AAS	% RSD[a]	*t**
1st S – Side 1	1	13.3	2.0	12.7	4.5	2.01
	2	63.7	6.7	62.3	6.9	2.14
	3	3.8	2.4	3.3	6.7	0.71
	4	13.5	4.6	14.2	1.1	0.26
1st S – Side 2	1	3.4	3.8	2.8	1.1	0.34
	2	37.6	5.3	39.4	2.6	0.26
	3	12.5	3.8	16.1	1.1	0.92
	4	12.7	3.8	13.5	3.0	0.51
2nd S – Side 1	1	8.4	1.99	7.4	3.1	0.64
	2	99.1	1.5	92.3	6.7	0.19
	3	16.1	4.1	13.7	3.2	0.91
	4	2.8	5.2	3.4	2.6	0.15
2nd S – Side 2	1	3.7	6.4	3.2	0.3	0.50
	2	43.3	3.3	46.8	1.8	0.31
	3	5.5	3.3	5.1	2.7	0.45
	4	10.6	4.1	11.5	3.8	0.24

[a] Calculated from $n = 5$.
*Student *t*-test – calculated, theoretical value 2.776 ($P = 0.05$).
S, semester. Sides 1 and 2 are different points in the water distributor.

the high amounts detected, that purified water may be subsequently polluted through contact with these sediments.

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