

The dosing accuracy of copper and silver ionisation systems: separate high purity copper and silver electrodes versus copper/silver alloys



Nikolaj Walraven^{a,*}, Wiebe Pool^b, Conrad Chapman^b

^a GeoConnect Sensing BV, Meester Dekkerstraat 4, 1901 PV, Castricum, the Netherlands

^b Holland Water BV, Nijendal 52, 3972 KC D Riebergen, the Netherlands

ARTICLE INFO

Article history:

Received 15 June 2015

Received in revised form 2 September 2015

Accepted 14 September 2015

Keywords:

Copper
Silver
Ionisation
Water
Treatment

ABSTRACT

Copper and silver ionisation is a widely accepted technique to abate and control *Legionella* bacteria in contaminated water. Currently two types of copper and silver ionisation systems are commercially available: (1) systems using separate high purity copper and silver electrodes and (2) systems using copper/silver alloys in various compositions. The aim of this study was to determine the dosing accuracy of these two distinguishable copper and silver ionisation systems. This study showed that both copper and silver can be dosed accurately, according to Faraday's law, with systems using separate high purity copper and silver electrodes as anodes. Systems with new copper/silver alloys (Alloys 70/30 and 90/10) as anodes can only dose copper in predictable quantities. With new copper/silver alloys, silver concentrations were under dosed (<20 µg/l Ag; minimum silver target level at outlets specified to control *Legionella* in water distribution systems). This is most likely caused by a difference in the efficiency of the electrolysis process of copper and silver in alloys. Silver is more oxidation and corrosion resistant than copper (more noble). The dosed silver concentrations with copper/silver alloys remained below the minimum recommended concentration for effective *Legionella* abatement, making alloys unsuitable especially when dosing directly into the water supply.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

The target organism *Legionella*, usually *L. pneumophila* serogroup 1, is the causative agent of Legionnaires' disease, a severe form of pneumonia, and may cause Pontiac disease, a self-limiting nonpneumonia illness [15,18,1]. Legionnaires' disease can be very serious and can cause death in up to 5–30% of cases [21,11]. *Legionella* outbreaks can, amongst others, occur in water distribution systems including drinking water, process water (e.g., cooling water), fountains and swimming pools. Aerosolized water droplets from these contaminated water systems pose significant health risks to people [9]. Because *Legionella* can cause devastating disease in humans (especially in immuno-suppressed patients), it is important to prevent water systems from becoming contaminated and to control the risk of exposure [10,1]. The control of hazardous pathogens, such as *Legionella* in water distribution systems and cooling towers, is therefore a priority for health authorities worldwide. A well-recognized disinfection method is copper and silver ionisation [19,13,18,26]. The method is based on channelling

the water through a device that applies low potential electricity to copper and silver electrodes. The positively charged copper and silver ions thus released, form electrostatic bonds with negatively charged sites found on bacterial cell walls. These electrostatic bonds create stresses leading to distorted cell wall permeability; coupled with protein denaturation this leads to cell lysis and cell death [25,1]. Importantly, some authors have demonstrated that these ions are able to penetrate the biofilms in which other bacteria, algae, protozoans, and fungi cohabit with *Legionella* species in water pipes [20,8]. The amount of copper and silver dosed must remain within a certain range for efficiency, and at the same time remain below the WHO and other guidelines [3]. Studies carried out in-vitro demonstrated that effective copper and silver concentrations (to inactivate *L. Pneumophila*) are 400 µg/l for copper and 40 µg/l for silver (amongst others [15,16,2]). The target concentrations for *Legionella* eradication are 200–400 µg/l and 20–40 µg/l, respectively [19,16,18]. The maximum permitted levels in drinking water in the Netherlands, and most other European countries, is 2000 µg/l copper [5,7] and 100 µg/l silver [4,30].

Currently there are various copper and silver ionisation systems available on the market. Two authorized types for treatment of drinking water in the Netherlands can be distinguished: (1) systems with separate high purity copper (>99.9 wt.%) and high purity

* Corresponding author.

E-mail address: n.walraven@geoconnect.nl (N. Walraven).

silver (>99.99 wt.%) electrodes and (2) systems with a copper/silver alloy (Cu (wt.)/Ag (wt.) 70/30). In other countries various copper/silver alloy compositions are applied (e.g.,: 50/50, 60/40, 70/30 and 90/10). To our knowledge, there are no open source publications available in which the dosing accuracy (the accuracy by which copper and silver can be dosed to drinking water; see Section 2.3 for details) of copper and silver ionisation systems is studied and reported, and in which the dosing accuracy of separate high purity copper and silver electrodes is compared with copper/silver alloys. In this study, we present results of theoretical considerations and practical experiments to establish the dosing accuracy of separate copper and silver electrodes and copper/silver alloys.

2. Methods and materials

2.1. Theoretical considerations

The electrolysis processes in copper and silver ionisation systems are based on Faraday's Laws of electrolysis. According to Faraday's 1st law of electrolysis 'the mass of a substance altered at an electrode during electrolysis is directly proportional to the quantity of electricity transferred at that electrode.' Quantity of electricity refers to the quantity of electrical charge, typically measured in coulomb. Faraday's 2nd law of electrolysis states that, 'for a given quantity of DC electricity (electric charge), the mass of an elemental material altered at an electrode is directly proportional to the element equivalent weight.' Faraday's laws can be summarized by,

$$m = \frac{(Q \times M)}{(F \times z)} \quad (1)$$

where m is the mass of the substance liberated at an electrode in grams, Q is the total electric charge passed through the substance in Coulombs or ampere second, F is the Faraday constant (96485 C/As for 1 g equivalent), M is the molar mass of the substance in g mol^{-1} and z is the substance's valency. In case of constant-current electrolysis, $Q = I \times t$, and with n (amount of substance in moles) = m/M , Eq. (1) becomes,

$$n = \frac{(I \times t)}{(F \times z)} \quad (2)$$

where I is the electric current in ampere and t is the total time the constant current was applied.

With Faraday's laws the amount of current needed to dose 400 $\mu\text{g/l}$ copper and 40 $\mu\text{g/l}$ silver to water is calculated (see Section 3.1). In addition the theoretical composition of the copper/silver alloys to dose the desired concentrations of copper and silver is calculated (see Section 3.1). However, a complicating factor with dosing copper and silver concentration using copper/silver alloys is the difference in standard potential ($E^\circ_{\text{Cu}} = 0.34$, $E^\circ_{\text{Ag}} = 0.80$, vs. SHE at 25 °C; [6]) of copper and silver within the alloy. According to the galvanic series (e.g. [12]), silver is more noble than copper (more oxidation and corrosion resistant), which implies that copper is preferably released from the alloy upon electrolysis. It is therefore assumed that ionisation with a new copper/silver alloy will lead to a relative enrichment of the more noble silver metal at the electrode surface during the ionisation process. This will result in a continuously changing alloy composition at the electrode surface in which the silver content will continuously increase. The rate of change depends on the electrolyte (e.g., treated drinking water and process water) in which the alloy is ionised and the difference in nobility between copper and silver present in the alloy.

2.2. Laboratory experiments

To determine the dosing accuracy of separate high purity copper (>99.9 wt.% Cu supplied by Staalmarkt) and silver (>99.99 wt.% Ag supplied by Thessco) electrodes and homogeneous copper/silver alloys (Alloys 70/30 and 90/10; standard alloy suppliers), 3 laboratory experiments were performed with new electrodes and alloys. The setup of these experiments is given in Table 1. Experiment 1–3 were performed in accordance to Faraday's law with a power supply with adjustable current regulator. Both copper and silver ionisation systems were connected via a bypass to the same water distribution system. It concerns a water distribution system in an office building in the Netherlands. The average composition of drinking water in the water distribution system – as specified by the water supply company – is pH 7.98, 42 mg/l Cl, 22 mg/l SO_4 , 21.6 mg/l Na, 0.87 mg/l K, 37.3 mg/l Ca, 4.52 mg/l Mg and 5.61 mg/l NO_3 [29]. The systems consist of a control unit with a programmable logic controller (PLC). The separate high purity copper and silver electrodes were placed in separate ionisation chambers (Table 1, experiment 1). Each ionisation chamber contained two electrodes of copper or silver. In most commercial ionisation equipment the polarity is periodically changed to prevent fouling. During polarity change the double layer on the electrode surface will be discharged and recharged. These processes cost a certain amount of Coulomb and this amount of Coulomb depends on the composition of the water and the electrode surface. The higher the ionic strength of the water and/or the higher the electrode surface, the higher the amount of Coulomb necessary to start generation of copper and silver ions by electrolysis. An important issue is that this amount is also not available for the ionisation processes. Polarity change of the separate electrodes (to prevent fouling) has been switched off during the tests because the experiments were conducted within a short period of time (few hours) and fouling did not occur. The copper/silver alloys were placed in a single ionisation chamber (Table 1, experiments 2 and 3). Also here, polarity change was switched off. In both copper and silver ionisation systems, water was channelled through the ionisation chamber(s) and low DC voltage was applied to the separate copper and silver electrodes or copper/silver alloys.

The copper and silver ionisations systems were set to effectively dose the copper and silver concentrations (set target values) as listed in Table 1. The actual dosed Cu and Ag concentrations, according to Faraday's law, were calculated according to Eqs. (3) and (4),

$$\text{Cu}_{\text{cal}} = \left(\frac{(I - 2)/f \times 60}{3.0389} \right) \quad (3)$$

$$\text{Ag}_{\text{cal}} = \left(\frac{(I - 2)/f \times 60}{0.8943} \right) \quad (4)$$

where Cu_{cal} and Ag_{cal} are the calculated dosed Cu and Ag concentrations in $\mu\text{g/l}$, I is the measured DC current in mA over the electrodes or alloy, f is the total flow through the electrode/alloy chamber in l/min, 60 is the conversion factor of seconds to minutes, 3.0389 is the amount of Coulomb (mAs) per μg Cu, 0.8942 is the amount of Coulomb (mAs) per μg Ag and 2 is a correction for the current measured through the electrodes in water in mA. Under the test conditions – temperature of $\sim 8^\circ\text{C}$ and conductivity of 320 $\mu\text{S/cm}$ (at 25 °C) – the electrolysis start at ≥ 2 mA current through the electrodes.

The current measurements ($\pm 2\%$) over the electrodes and alloys is the average current of a PWM (Pulse Width Modulation) current. The set currents over the over the copper and silver electrodes and copper/silver alloys during the experiments are automatically adjusted for variations in water flow. A pair of electromagnetic flow

Table 1

Setup of the laboratory experiments to determine the dosing accuracy of separate high purity copper and silver electrodes and copper/silver alloys.

Experiment	Cu/Ag ionisation system	Electrodes	Average flow rate per cell (l/min)	Set Cu and Ag concentrations ($\mu\text{g/l}$)		Set current strength (mA/l/min)	
				Cu	Ag	Cu	Ag
1	2 Separate cells with pairs of Cu and Ag electrodes (adjusted settings)	Separate:	7.5	0	0	0	0
		Cu (>99.9 wt.%)	Total 15 (l/min)	125	6	6.2	0.2
		Ag (>99.99 wt.%)		500	35	25.3	0.55
2	Cu/Ag alloy (adjusted settings)	Alloy 70/30:	8.4	600	50	31.4	1.0
		Cu (70 wt.%)		200	–	14.2	–
		Ag (30 wt.%)		400	–	29.0	–
3	Cu/Ag alloy (adjusted settings)	Alloy 90/10:	8.4	800	–	57.3	–
		Cu (90 wt.%)		200	–	14.5	–
		Ag (10 wt.%)		400	–	28.9	–
				800	–	57.4	–

meters with a resolution of 0.1 l/min and an accuracy of $\pm 4\%$ was used to determine the water flow in all experiments.

With the separate copper and silver electrode setup (experiment 1), copper and silver concentrations can be dosed (controlled) independently. With the copper/silver alloys setup (experiments 2 and 3), this is not possible. In this study, it was decided to dose the copper concentrations with the copper/silver alloys at the desired concentration (using Eq. (3)). This means that the silver concentrations dosed with copper/silver alloys depend entirely on the set target values for copper. The theoretically dosed silver concentrations with copper/silver alloys are calculated using Eq. (4). This is under the assumption that copper and silver ionisation in copper/silver alloys behaves the same as in separate high purity copper and silver electrodes. According to the galvanic series this is, however, not the case (see Section 2.1).

2.3. Sampling and analyses

The copper and silver concentrations dosed to drinking water (average hardness = 5.5°D ; average electrical conductivity = $320 \mu\text{S/cm}$ at 25°C) with the separate high purity copper and silver electrodes were measured by 2 accredited laboratories: Vitens (further referred to as Lab 1) and KIWA (further referred to as Lab 2). These analyses were conducted in the framework of a legally required KIWA test to obtain a product certificate that allows usage of copper and silver ionisation to abate *Legionella* contaminations in drinking water and cooling water in the Netherlands [14]. The copper and silver concentrations dosed to drinking water (hardness = 5.5°DH ; electrical conductivity = $320 \mu\text{S/cm}$ at 25°C) with the copper/silver alloys were not part of the KIWA test and were analysed by Vitens.

Both laboratories (KIWA and Vitens) are accredited according to NEN-EN-ISO/IEC 17025:2005 [22]. Sampling (a.o., flushing time of the system, sampling frequency, etc.) was performed in accordance with the Dutch assessment protocol for alternative techniques for *Legionella* prevention [14]. Sample pre-treatment (on-site filtration and acidification of the water samples) and analyses of the copper and silver concentrations were performed in accordance with NEN-EN-ISO 17294-1 [23] and NEN-EN-ISO 17294-2 [24]. The limit of detection (LOD) for copper and silver is $5 \mu\text{g/l}$ and $1 \mu\text{g/l}$ respectively.

2.4. Data analysis

Dosing accuracy of copper and silver ionisation with high purity Cu and Ag electrodes and Cu/Ag alloys is calculated according to Eq. (5).

$$\frac{[C]_{\text{laboratory}}}{[C]_{\text{cal}}} \times 100\% \quad (5)$$

where $[C]$ is the Cu or Ag concentration in $\mu\text{g/l}$, $[C]_{\text{laboratory}}$ are measured concentrations from accredited laboratory experiments and $[C]_{\text{cal}}$ are the calculated dosed Cu and Ag concentrations in $\mu\text{g/l}$ according to Eqs. (3) and (4).

Linear regressions were performed with the software package StatSoft 12 from Statistica to determine the correlation coefficient (R^2) and significance level (P value) between the dosed Cu and Ag concentrations and the measured Cu and Ag concentration in accredited laboratories. Values 'less than' the detection limit are, following a simple substitution method [27], replaced by $\frac{3}{4}$ times the detection limit.

3. Results

3.1. Theoretical weight ratio of copper/silver alloys

Faraday's laws of Electrolyses was used to calculate the theoretical weight ratio of copper/silver alloys (Eqs. (1) and (2)). When dosing $400 \mu\text{g/l}$ Cu and $40 \mu\text{g/l}$ Ag to water and assuming a 100% ionisation efficiency for both Cu and Ag, Eq. (2) becomes,

$$\frac{I_{\text{Cu}}}{I_{\text{Ag}}} = \frac{(n \times z)_{\text{Cu}}}{(n \times z)_{\text{Ag}}} = \frac{(2 \times 6.30\text{E-}06)}{(1 \times 3.71\text{E-}07)} = \frac{34}{1} \quad (6)$$

where I is the electric current, n is the amount of substance in moles and z the valency of the substance. Eq. (6) shows that a theoretical current ratio of 34/1 is necessary to dose $400 \mu\text{g/l}$ Cu and $40 \mu\text{g/l}$ Ag to water. This can be achieved with an alloy having a composition of 97 wt.% copper and 3 wt.% silver (see also [28]). An alloy with this composition has not been used in this study, because this alloy is as far as known not applied in any copper and silver ionisation system. The alloys that have been tested in this study are listed in Table 1. It is noted, however, that this is the theoretical weight ratio. Since the efficiency of the electrolysis process of copper is different from silver (galvanic series) and also depends on the water composition in which is dosed, the 'real' weight ratio to be able to dose $400 \mu\text{g/l}$ Cu and $40 \mu\text{g/l}$ Cu to *Legionella* contaminated water might differ.

3.2. Copper and silver ionisation under laboratory conditions: separate electrodes versus alloys

Tables 2–4 summarise the analytical results of the copper/silver experiments

3.2.1. Separate high purity Cu and Ag electrodes (experiment 1)

With the separate high purity copper electrodes a positive ($R^2 = 0.99$) and significant ($P < 0.01$) correlation is observed between the theoretically dosed copper concentrations (Eq. (3)) and the copper concentrations in drinking water measured by the accredited

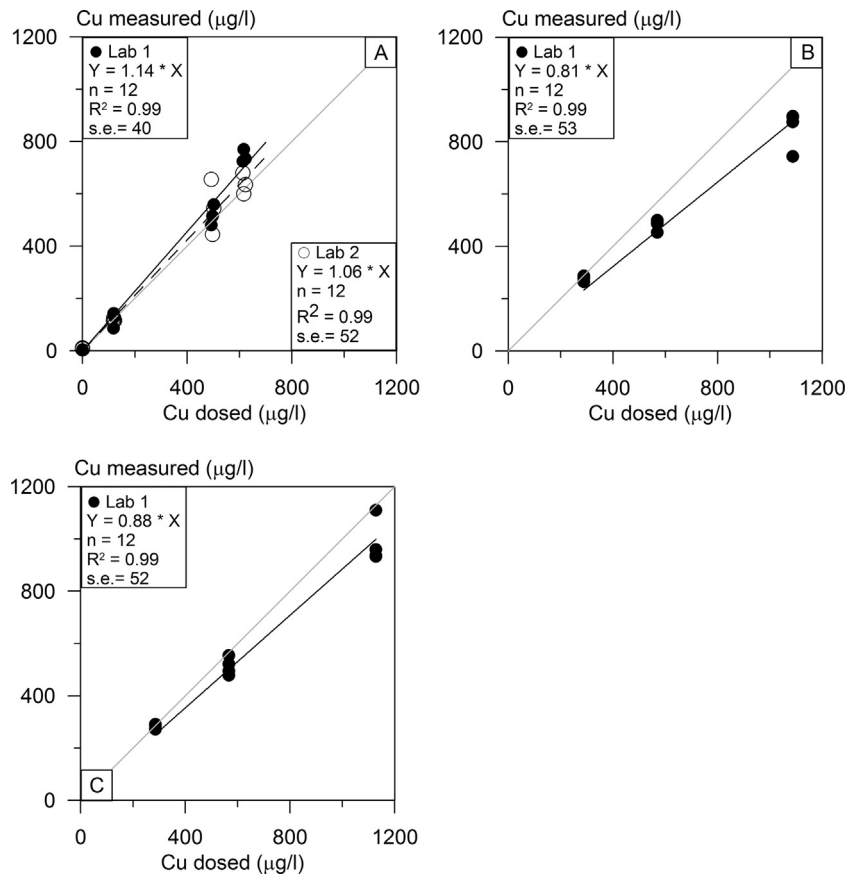


Fig. 1. Theoretically dosed Cu concentrations (Eq. (3)) versus measured Cu concentrations (accredited laboratory) using copper and silver ionisation with (A) separate high purity Cu (>99.9 wt.%) and Ag (>99.99 wt.%) electrodes, (B) a 70:30 wt.% copper/silver alloy and (C) a 90:10 wt.% copper/silver alloy.

laboratories (Fig. 1A; for both Lab 1 and Lab 2). The average dosing accuracy for copper according to the results of Lab 1 and Lab 2 is $108\% \pm 16\%$ (1 SD) and $104\% \pm 13\%$ (1 SD), respectively. The average dosing accuracy for the separate copper electrodes, when combining the results of both laboratories, is $106\% \pm 14\%$ (1 SD).

A positive ($R^2 = 0.96$ for Lab 1; $R^2 = 0.97$ for Lab 2) and significant ($P < 0.01$) correlation is also observed between the theoretically dosed silver concentrations (Eq. (4)) with the separate high purity silver electrodes and the measured silver concentrations in drinking water (Fig. 2A; for both Lab 1 and Lab 2). The average dosing accuracy for silver according to the results of Lab 1 and Lab 2 is $62\% \pm 13\%$ (1 SD) and $135\% \pm 49\%$ (1 SD) respectively. The average dosing accuracy for the separate silver electrodes, when combining the results of both laboratories, is $99\% \pm 51\%$ (1 SD).

3.2.2. Copper/silver alloys (experiments 2 and 3)

With both alloys a positive ($R^2 = 0.99$) and significant ($P < 0.01$) correlation is observed between the theoretically dosed (Eq. (3)) and measured copper concentration in drinking water (Fig. 1B and C). The achieved average dosing accuracy with Alloy 70/30 is $87\% \pm 9\%$ (1 SD). For Alloy 90/10 the average dosing accuracy is $92\% \pm 7\%$ (1 SD).

Although a positive ($R^2 = 0.88$) and significant ($P < 0.01$) correlation is observed between the theoretically dosed silver concentration (Eq. (4)) with Alloy 70/30 (Fig. 2B), the dosing accuracy is $<0.4\%$ at theoretically dosed concentrations of $262 \mu\text{g/l}$ and $1.0\% \pm 0.5\%$ (1 SD) at concentrations of 518 and $990 \mu\text{g/l}$ Ag (Table 3). The measured silver concentrations (accredited laboratory) in drinking water treated with Alloy 70/30 varied from <1 to $10 \mu\text{g/l}$ (Table 3). The measured silver concentrations in drinking water treated with Alloy 90/10 were all $<1 \mu\text{g/l}$ (Table 4, Fig. 2C).

Linear regression could not be performed for this experiment (due to the lack of variance in the data). The dosing accuracy for silver for Alloy 90/10 varies between $<0.3\%$ and $<1.2\%$.

4. Discussion

The recommended concentrations for the eradication of *Legionella* bacteria with copper and silver ionisation are $200\text{--}400 \mu\text{g/l}$ for copper and $20\text{--}40 \mu\text{g/l}$ for silver [19,16,18]. At lower copper and/or silver concentrations total eradication (successful abatement) of *Legionella* bacteria is not guaranteed. However, lower copper and silver concentrations have proven effective after initial abatement of *Legionella* with copper and silver ionisation with the recommended dosage (so-called residual effect) [19,20,18]. For the highest efficacy (eradication of *Legionella*), however, the amount of copper and silver dosed should remain within the recommended concentrations. In addition, copper and silver concentrations must remain below the maximum permitted levels for drinking water. In the Netherlands, and most other European countries, these levels are $2000 \mu\text{g/l}$ for copper [5,7] and $100 \mu\text{g/l}$ for silver [4,30].

This study shows that copper concentrations in the range of 0 to $\sim 1000 \mu\text{g/l}$ can be dosed accurately with both separate high purity copper electrodes and copper/silver alloys (Alloys 70/30 and 90/10) (Figs. 1 and 2). The best accuracy was achieved with the separate high purity copper electrodes (on average $106\% \pm 14\%$ (1 SD)). With both copper/silver alloys, copper was slightly under dosed (Fig. 1): measured copper concentration were on average 13% and 8% lower than theoretically dosed with Alloys 70/30 and 90/10, respectively. This can however be adjusted by slightly increasing the current strength applied to the copper/silver alloys.

Table 2

Results of the theoretically dosed and measured copper and silver concentrations, dosed with a copper and silver ionisation system using separate high purity copper (>99.9 wt.%) and silver (>99.99 wt.%) electrodes.

Test	Flow (l/min)	Set target doses		Average measured DC current		Calculated doses (Eqs. (3) and (4))		Lab 1 results (measured)		Lab 2 results (measured)		Dosing accuracy (%) (Eq. (5))			
		Cu ($\mu\text{g/l}$)	Ag ($\mu\text{g/l}$)	Cu (mA)	Ag (mA)	Cu ($\mu\text{g/l}$)	Ag ($\mu\text{g/l}$)	Cu ($\mu\text{g/l}$)	Ag ($\mu\text{g/l}$)	Cu ($\mu\text{g/l}$)	Ag ($\mu\text{g/l}$)	Cu Lab 1	Cu Lab 2	Ag Lab 1	Ag Lab 2
1.1.1	15.1	500	25	382	8.2	497	28	515	16.6	445	45	104	90	59	161
1.1.2	15.1	500	25	385	8.4	501	28	559	19.6	545	30	112	109	70	107
1.1.3	15.1	500	25	378	8.2	492	28	481	23.0	655	25	98	133	82	89
1.1.4	15.1	600	50	473	15.0	616	58	771	35.4	600	57	125	97	61	98
1.2.1	15.1	600	50	471	15.2	613	59	725	34.6	680	50	118	111	59	85
1.2.2	15.1	600	50	478	15.5	622	60	735	24.8	635	65	118	102	41	108
1.2.3	15.1	125	6	95	3.1	122	5	129	2.5	115	10	106	94	50	200
1.2.4	15.1	125	6	93	3.1	119	5	143	3.8	125	7.9	120	105	76	158
1.3.1	15.1	125	6	92	3.0	118	4	86	2.4	115	8.5	73	97	60	213
1.3.2	15.1	0	0	0	0	0	0	<5	1.4	7	2.0	–	–	–	–
1.3.3	15.1	0	0	0	0	0	0	5	<1	8	3.1	–	–	–	–
1.3.4	15.1	0	0	0	0	0	0	<5	1.3	11	0.2	–	–	–	–

Table 3

Results of the theoretically dosed and measured copper and silver concentrations, dosed with a copper and silver ionisation system using 70:30 wt.% copper/silver.

Test	Flow (l/min)	Set target doses		Average measured DC current		Calculated doses (Eqs. (3) and (4))		Lab 1 results (measured)		Dosing accuracy (%) (Eq. (5))	
		Cu ($\mu\text{g/l}$)	Ag ($\mu\text{g/l}$)	Alloy (mA)	Cu ($\mu\text{g/l}$)	Ag ($\mu\text{g/l}$)	Cu ($\mu\text{g/l}$)	Ag ($\mu\text{g/l}$)	Cu Lab 1	Ag Lab 1	
2.1.1	8.1	200	–	120	–	288	262	265	<1	92	<0.4
2.1.2	8.1	200	–	120	–	288	262	284	<1	99	<0.4
2.1.3	8.1	200	–	120	–	288	262	279	<1	97	<0.4
2.1.4	8.1	200	–	120	–	288	262	287	<1	100	<0.4
2.2.1	8.4	400	–	244	–	569	518	496	1.52	87	0.3
2.2.2	8.4	400	–	244	–	569	518	487	6.75	86	1.3
2.2.3	8.4	400	–	244	–	569	518	500	9.19	88	1.8
2.2.4	8.4	400	–	244	–	569	518	454	6.73	80	1.3
2.3.1	8.7	800	–	481	–	1087	990	744	8.91	68	0.9
2.3.2	8.7	800	–	481	–	1087	990	895	9.89	82	1.0
2.3.3	8.7	800	–	481	–	1087	990	898	7.43	83	0.8
2.3.4	8.7	800	–	481	–	1087	990	876	6.35	81	0.6

One current strength in mA/l/min is set during the test with alloys. The separated target doses of copper and silver with alloys are uncertain, so an initial current strength of ca. 7 mA/ (100 $\mu\text{g/l}$ Cu) is applied.

Table 4

Results of the theoretically dosed and measured copper and silver concentrations, dosed with a copper and silver ionisation system using 90:10 wt.% copper/silver alloy.

Test	Flow (l/min)	Set target doses		Average measured DC current		Calculated doses (Eqs. (3) and (4))		Lab 1 results (measured)		Dosing accuracy (%) (Eq. (5))	
		Cu ($\mu\text{g/l}$)	Ag ($\mu\text{g/l}$)	Alloy (mA)	Cu ($\mu\text{g/l}$)	Ag ($\mu\text{g/l}$)	Cu ($\mu\text{g/l}$)	Ag ($\mu\text{g/l}$)	Cu Lab 1	Ag Lab 1	
3.1.1	8.3	200	–	122	–	285	84	272	<1	95	<1.2
3.1.2	8.3	200	–	122	–	285	84	274	<1	96	<1.2
3.1.3	8.3	200	–	122	–	285	84	292	<1	102	<1.2
3.1.4	8.3	200	–	122	–	285	84	286	<1	100	<1.2
3.2.1	8.4	400	–	243	–	566	167	522	<1	92	<0.6
3.2.2	8.4	400	–	243	–	566	167	555	<1	98	<0.6
3.2.3	8.4	400	–	243	–	566	167	479	<1	85	<0.6
3.2.4	8.4	400	–	243	–	566	167	496	<1	88	<0.6
3.3.1	8.4	800	–	482	–	1128	332	960	<1	85	<0.3
3.3.2	8.4	800	–	482	–	1128	332	1110	<1	98	<0.3
3.3.3	8.4	800	–	482	–	1128	332	933	<1	83	<0.3
3.3.4	8.4	800	–	482	–	1128	332	937	<1	83	<0.3

One current strength in mA/l/min is set during the test with alloys. The separated target doses of copper and silver with alloys are uncertain, so an initial current strength of ca. 7 mA/ (100 $\mu\text{g/l}$ Cu) is applied.

Unlike copper, dosing silver in the desired range of 0–60 $\mu\text{g/l}$ could only be achieved accurately with the high purity separate silver electrodes (on average $99\% \pm 51\%$ (1 SD)) (Fig. 2). However, it is noted that the silver concentrations determined by the 2 accredited laboratories differ substantially (Fig. 2). The reason for the observed differences is unknown (drinking water samples were filtered, acidified, split in 2 sub samples and send to the 2 different

laboratories). According to the results of Lab 1 silver concentration were under dosed ($\sim 38\%$) with the high purity silver electrodes whereas according to the results of Lab 2 silver concentration were overdosed ($\sim 35\%$) (Fig. 2).

The dosing accuracy for silver with both tested copper/silver alloys is low: $<0.4\text{--}1.0\% \pm 0.5\%$ for Alloy 70/30 (absolute silver concentrations were $<1\text{--}10 \mu\text{g/l}$) and $<0.3\text{--}1.2\%$ for Alloy 90/10

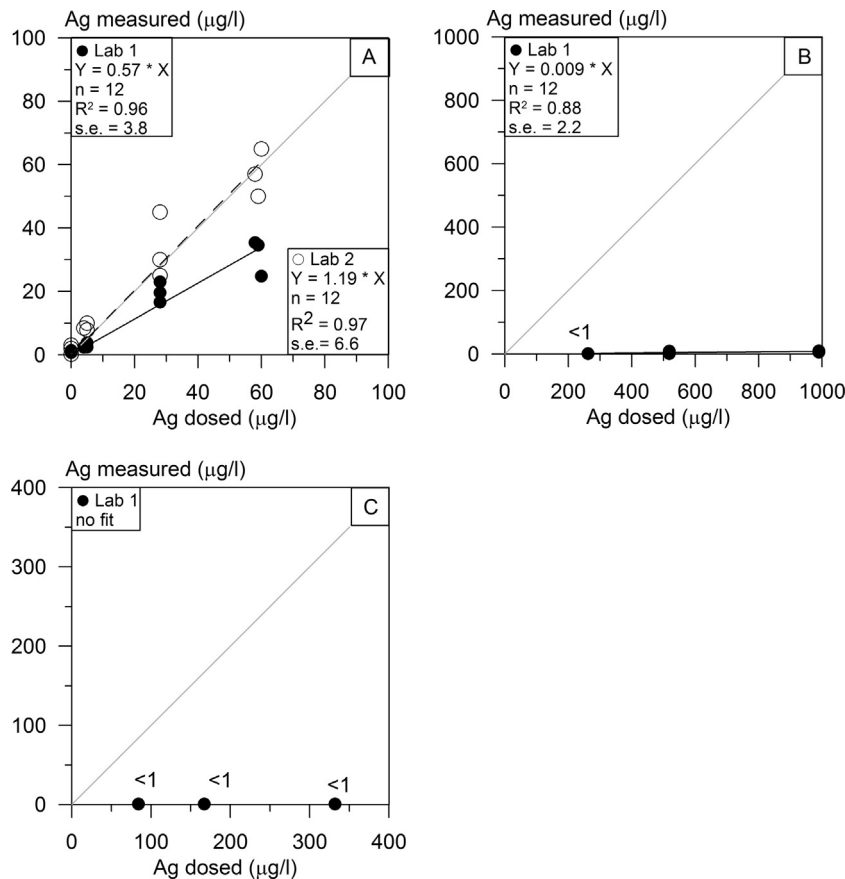


Fig. 2. Theoretically dosed Ag concentrations (Eq. (3)) versus measured Ag concentrations (accredited laboratory) using copper and silver ionisation with (A) separate high purity Cu (>99.9 wt.%) and Ag (>99.99 wt.%) electrodes, (B) a 70:30 wt.% copper/silver alloy and (C) a 90:10 wt.% copper/silver alloy.

(absolute silver concentrations were $<1 \mu\text{g/l}$) (Fig. 2). Although the chemical composition of Alloy 90/10 (Table 1) is closest to the theoretical weight ratio of 97 wt.% copper and 3 wt.% silver for the theoretical dosing of $400 \mu\text{g/l}$ Cu and $40 \mu\text{g/l}$ Ag (see Section 3.2.1), it shows the lowest dosing accuracy for silver. This is most likely caused by difference in the efficiency of the electrolysis process of copper and silver (galvanic series). Since silver is more noble than copper, new alloys consisting of 90 wt.% copper and 10 wt.% silver (Alloy 90/10) will almost exclusively release the less nobler copper ions upon ionisation. The treated drinking water will hardly contain silver ions when starting with a new alloy electrode, which is observed in Fig. 2C. It is assumed (this is not tested in this study) that after using Alloy 90/10 for a certain time, the copper content at the alloys' surface will be depleted enough that release (dosing) of silver ions will occur. This makes the dosing ratio between copper and silver ions time dependent and it is therefore not possible to constantly dose the recommended concentrations of $200\text{--}400 \mu\text{g/l}$ Cu and $20\text{--}40 \mu\text{g/l}$ Ag during drinking water treatment. This will result in under dosing of silver ions when starting with a fresh copper/silver alloy and most likely overdosing of silver ions with ageing of the copper/silver alloy. The observed under dosing of silver when using new copper/silver alloys is less pronounced with Alloy 70/30 than with Alloy 90/10 (Fig. 2B and C). This is caused by the relative higher silver to copper content in Alloy 70/30 (Table 1). However, the recommended minimum concentrations of $20 \mu\text{g/l}$ Ag for successful eradication of *Legionella* bacteria was not achievable with any of the tested alloys (Tables 3 and 4).

Copper and silver ions can be dosed most accurately when using copper and silver ionisation systems which utilise high purity separate copper and silver electrodes. These systems can be used both

for directly dosing copper and silver ions to drinking water and indirect dosing in to water storage tanks before supplying drinking water to the desired locations. According to our study copper and silver ionisation systems using copper/silver alloys (Alloys 90/10 and 70/30) are not capable of dosing silver accurately to drinking water, which can result in both under dosing of silver when starting with new copper/silver alloys and most likely overdosing with ageing of the copper/silver alloys. With Cu/Ag alloys there is no control of current separately for each element and therefore, there is no control over ionic release. In addition, due to the lack of control of the current passing between Cu/Ag alloys, fouling of Cu/Ag alloys is most likely also more difficult to control.

In United States Patent 4680114 [28] is claimed that with an alloy of 97 wt.% copper and 3 wt.% silver, $500\text{--}800 \mu\text{g/l}$ copper and about $10 \mu\text{g/l}$ silver can be dosed particularly, but not exclusively, to water in swimming pools. In our study, dosing to swimming pool water was not studied. However, based on our experiments, direct and accurate dosing of copper and silver to drinking water in the ranges claimed by United States Patent 4680114 [28], with copper/silver alloys, seems unfeasible (especially for silver). It could be argued that when dosing in to swimming pools or large water storage tanks that the different dissolution rates of the metals from the alloy will average out, creating an appearance of good dosing. However, in these systems the residence time of water in the buffer tanks would be critical and if not totally refreshed with an hourly rate (or maybe less), then dissolved (active) silver concentration might drop quickly, especially where there are chloride ions present (complexation and precipitation). Lin et al. [17] demonstrated that when chloride concentrations increase, the availability of positively charged silver ions is reduced due to complexation

reactions. This suggests that chloride concentrations in water may possibly decrease the availability of silver cations and reduce its biocidal potential [17]. To avoid silver complexation, residence times should be minimized and therefore direct dosing is preferred over indirect dosing.

This article shows that a high 'direct' dosing accuracy is achieved with separate high purity copper and silver electrodes (as also seen by Bedford [1]). Effective and constant silver concentrations cannot be guaranteed when dosing silver ions to drinking water with copper/silver alloys.

5. Conclusions

Copper can be dosed accurately both with high purity copper electrodes and new copper/silver alloys (Alloys 70/30 and 90/10). This is not the case for silver. Silver can only be dosed accurately with copper and silver ionisation systems using separate high purity silver electrodes. With new copper/silver alloys (Alloys 70/30 and 90/10) the actual dosed silver concentrations (laboratory data) are much lower than the theoretical dosed concentrations (under dosing). The measured silver concentrations are even lower than the minimum recommended concentration of 20 µg/l silver for the effective abatement of *Legionella* bacteria. This is most likely caused by a difference in the efficiency of the electrolysis process of copper and silver. Since silver is more noble than copper, new alloys consisting of 70 or 90 wt.% copper and 30 or 10 wt.% silver will almost exclusively release the less nobler copper ions first. This makes copper/silver alloys unsuitable for accurate direct dosing of copper and silver to drinking in the recommended concentration range of 200–400 µg/l copper and 20–40 µg/l silver. Copper and silver ionisation using separate copper and silver electrodes is the most effective system to dose copper and silver ions to *Legionella* contaminated water and is therefore preferred over copper/silver alloys.

References

- [1] B. Bedford, *Legionella* control in water systems using copper and silver ion generation systems, in: PhD Thesis, Cranford University, Institute of Bioscience and Technology, 2012.
- [2] Building Services Research and Information Services (BSRIA) Technical notes TN6/96, Ionisation water treatment for hot and cold water services, 1996.
- [3] CORDIS, European Union, SILCO Report Summary, <<http://cordis.europa.eu/result/rcn/58257.pl.html>>, 2014 (accessed 08.14).
- [4] CTGB, <<http://www.ctgb.nl/toelatingen/toelating?id=13292>>, 2015 (accessed 08.15).
- [5] Dutch Drinking Water Act, <http://wetten.overheid.nl/BWBR0030111/geldigheidsdatum_27-08-2015#Hoofdstuk1>, 2015 (accessed 08.15).
- [6] D.D. Ebbing, General Chemistry, 3rd ed., Houghton Mifflin, 1990.
- [7] E.U. Drinking Water Directive, Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption, Off. J. Eur. Communities (1998), 5.12.98.
- [8] M. Exner, A. Kramer, J. Lajoie, J. Gebel, S. Engelhart, P. Hartemann, Prevention and control of health care-associated waterborne infections in health care facilities, Am. J. Infect. Control 33 (suppl. 1) (2005) S26–S40.
- [9] B.S. Fields, R.F. Benso, R.E. Besser, *Legionella* and Legionnaires' disease: 25 years of investigation, Clin. Microbiol. Rev. 15 (2002) 506–526.
- [10] D.C.C. Greenberg, R. Chiou, T.C. Famigilletti, T.C. Lee, V.L. Yu, Problem pathogens: paediatric legionellosis implications for improved diagnosis, Lancet Infect. Dis. 6 (2006) 529–535.
- [11] R.B. Hubbard, R.M. Mathus, J.T. MacFarlane, Severe community-acquired *Legionella pneumoniae*: treatment, complications and outcome, Q. J. Med. 86 (5) (1993) 327–332.
- [12] D.A. Jones, Principles and Prevention of Corrosion, 2nd ed., Prentice Hall, New Jersey, 1996.
- [13] KIWA Water Research (KWR), Evaluatie van praktijktesten met alternatieve technieken voor Legionella preventie, Koper/zilver-ionisatie, anodische oxidatie (waaronder elektrodiagramanalyse), pasteurisatie en ultrafiltratie, KWR 05.066, Nieuwegein, Nederland, 2006.
- [14] KIWA, Beoordelingsrichtlijn voor het Kiwa-attest met productcertificaat voor legionellapreventie met alternatieve technieken, Deel 2: Elektrochemische technieken. BRL-K14010-2/01, 2009-2-24. <<http://www.kiwa.nl/upload/BRL/K14010-2.pdf>>, 2009 (accessed 01.15).
- [15] L.K. Landeen, M.T. Yahya, C.P. Gerba, Efficacy of copper and silver ions and reduced levels of free chlorine in inactivation of *Legionella pneumophila*, Appl. Environ. Microbiol. 55 (1989) 3045–3050.
- [16] Y.E. Lin, R.D. Vidic, J.E. Stout, V.L. Yu, Individual and combined effects of copper and silver ions on inactivation of *Legionella pneumophila*, Water Res. 30 (8) (1996) 1905–1913.
- [17] Y.E. Lin, R.D. Vidic, J.E. Stout, V.L. Yu, Negative effect of high pH on biocidal efficacy of copper and silver ions in controlling *Legionella pneumophila*, Appl. Environ. Microbiol. 68 (2002) 2711–2715.
- [18] Y.E. Lin, J.E. Stout, M. Boldin, J. Rugh, W.F. Diven, V.L. Yu, Controlling *Legionella* in hospital drinking water: an evidence-based review of disinfection methods, Infect. Control Hosp. Epidemiol. 32 (2011) 166–173.
- [19] Z. Liu, J.E. Stout, L. Tedesco, M. Boldin, C. Hwang, W.F. Diven, V.L. Yu, Controlled evaluation of copper-silver ionization in eradicating *Legionella* from a hospital water distribution system, J. Infect. Dis. 169 (1994) 919–922.
- [20] Z. Liu, J.E. Stout, M. Boldin, J. Rugh, W.F. Diven, V.L. Yu, Intermittent use of copper-silver ionization for *Legionella* control in water distribution systems: a potential option in buildings housing individuals at low risk of infection, Clin. Infect. Dis. 26 (1998) 138–140.
- [21] B.J. Marston, H.B. Lipman, R.F. Breiman, Surveillance for Legionnaires' disease—risk factors for morbidity and mortality, Arch. Intern. Med. 154 (21) (1994) 2417–2422.
- [22] NEN, <<https://www.nen.nl/NEN-Shop/Norm/NENENISOIEC-170252005-en.htm>>, 2015 (accessed 05.15).
- [23] NEN, <<https://www.nen.nl/NEN-Shop/Norm/NENENISO-1729412006-en.htm>>, 2015 (accessed 05.15).
- [24] NEN, <<https://www.nen.nl/NEN-Shop/Norm/NENENISO-1729422004-en.htm>>, 2015 (accessed 05.15).
- [25] M.L. Pedro-Botet, I. Sanchez, M. Sabria, N. Sopena, L. Mateu, M. García-Núñez, C. Rey-Joly, Impact of copper and silver ionization on fungal colonization of the water supply in health care centers: implications for immunocompromised patients, Clin. Infect. Dis. 45 (2007) 84–86.
- [26] RIVM, J.A.C. Schalk, A.A. Bartels, A.M. De Roda Husman, Effectiviteit van beheer technieken voor Legionella in drinkwaterinstallaties, RIVM rapport 703719078, Bilthoven, Netherland, 2012.
- [27] R.F. Sanford, C.T. Pierson, R.A. Crovelli, An objective replacement method for censored geochemical data, Math. Geol. 25 (1993) 59–80.
- [28] United States Patent, Water purification apparatus, Patent number 4680114, 1987.
- [29] Vitens, <http://www.vitens.nl/overvitens/water/waterkwaliteit/Waterkwaliteit/WZ02_Pb.%20Driebergen.PDF>, 2015 (accessed 08.15).
- [30] WHO, World Health Organization. Guidelines for Drinking Water Quality, 4th ed., <http://www.who.int/water_sanitation_health/publications/2011/dwq-guidelines/en/>, 2011 (accessed 08.15).