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PEER-REVIEWED PAPER

Rinsing Properties of Inorganic Components from a Disinfection Line-Cleaner

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ABSTRACT

Beverage installations are generally cleaned and sanitized with alkaline or, optionally, oxidizing disinfection cleaners. Since any contact of cleaner residue with the dispensed beverage has to be avoided, a sufficient amount of rinse water is critical. In the current study, rinsing properties and correct volumes of rinse water were determined by using an acetic acid leaching method and inorganic trace analysis (inductively coupled plasma mass spectrometry [ICP-MS]). Analytical results were confirmed by means of electron beam microanalysis. Cleaning was carried out with new stainless steel and polyethylene tubing and an inorganic line-cleaning product at an elevated application concentration. Results of trace analysis from the leaching solution were compared with international drinking water and with dose that is lethal to 50% of test subjects (LD_{50}) limit concentrations; correct amounts of rinse water were derived from these data.

Keywords: alkaline cleaning agents, beverage line-cleaning, permanganate ion, persulfate ion, polyethylene tubing, stainless steel coolers

SÍNTESIS

Instalaciones de bebidas son normalmente lavados y saneados con materiales desinfectantes alcalinos u oxidantes. En cuanto se debe evitar cualquier contacto del residuo desinfectante con la bebida siendo servida, es imprescindible utilizar una cantidad suficiente de agua de enjuague. En este estudio se determinaron las propiedades de enjuague y el volumen necesario de agua de enjuague para un producto inorgánico de limpieza-en-línea, a un nivel de concentración más elevado de lo normal, después de limpiar una instalación de acero inoxidable y tubería de polietileno; esto se determinó utilizando un método de extracción con ácido acético y análisis de trazas inorgánicas (espectrometría de masa de plasma acoplado inductivamente [ICP-MS, por sus siglas en inglés]). Los resultados analíticos fueron confirmados mediante un microanálisis por rayos de electrones. Los resultados del análisis de trazas en la solución de extracción se compararon con normativas internacionales para agua potable y con concentraciones límites letales para 50% de sujetos testados (LD_{50}); partiendo de estos datos, se calculó la cantidad de agua de enjuage necesario.

Palabras claves: agentes de limpieza alcalinas, limpieza de líneas para bebidas, el ión de permanganato, el ión de persulfato, tubería de polietileno, enfriadores de acero inoxidable

Introduction

Because of the nature of the formed deposits, mainly product residue, proteins, and biomass plus metabolic products (usually referred to as "biofilms"), alkaline cleaning is state of the art for the maintenance of beverage lines. If powerful oxidizers are present, the cleaning effect can be enhanced by an oxidative breakup of large organic molecules. Water solubility is also improved by the introduction of electro-negative groups into the organic matter. The observed oxidative effects are dependent not only on the electrochemical potential of the oxidizer but also on the decomposition speed and reaction rates when in contact with reducing substances. This reaction is usually accelerated in an alkaline environment (neutralization of hydrogen ions formed by the oxidation process) and by specific catalysts. In addition, oxidizing action can enhance the biocidal properties of the cleaning agent, thus delaying the formation of new biofilms.

Although caustic substances and oxidizers are highly incompatible with beverages, there is little knowledge relative to chemical residuals remaining after the cleaning of nonaccessible parts of installations. The optimum amount of rinse water is usually unknown and is usually estimated. Simple pH testing (color indicator strips) can help, but the sensitivity of this method is limited and strongly dependent on the tap water's buffer capacity (hardness). Conductivity testing is more sensitive, but the equipment is costly and has not yet been widely used in beverage line-cleaning applications.

The object of this study was to determine the correct amounts of rinse water for a simple, exclusively inorganic, disinfection line-cleaner for beverage installations. The removal of chemical residues left by the cleaning agent was carried out by action of a leaching solution that had a composition comparable to that of typical beverages (e.g., beer and carbonated soft drinks), in particular with respect to the leaching potential for inorganic/ionic chemicals to leach from stainless steel or polyethylene surfaces. The composition incorporated the following.

1. A pH similar to that of beverages leads to the neutralization (carbonates and acetates are formed) of the caustic components and thus suppresses their wetting properties.

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2. pH also determines the degree of hydrolysis and, consequently, the water solubility of several chemical compounds (particularly for phosphates).
3. Overall ionic strength is also adjusted to a level similar to that of a beverage, modifying its water structure and properties as a solvent.
4. Acetic acid introduces chelating properties (affecting metal ions, in particular manganese) similar to those of beverages; the latter usually contain considerable amounts of organic chelates (e.g., citrate and ascorbic acid).

Since there are no legal limits for residue of most of the components used in inorganic cleaning agents, World Health Organization (WHO) drinking water guidelines, as well as the dose that is lethal to 50% of test subjects (LD_{50}) levels of the pure chemicals, were used for comparison.

Materials and Methods

Cleaning Agent

The disinfection beverage line-cleaner with color indication (solid powder product TM DESANA MAX; Thonhauser Corp., Vienna, Austria [3]) had a concentration of 16.5 g per L of demineralized water (= twofold the recommended application concentration [5]). The main components, according to information from the manufacturer, are sodium hydroxide, sodium peroxodisulfate, and potassium permanganate.

Beverage Line Construction Materials

A stainless steel coil (7-mm inside diameter; 1.4301 chromium-nickel steel) from a beverage cooler (sample code ST) was used. Also used was SK-approved polyethylene tubing (VALPAR Superflexmaster, 7-mm inside diameter; Valpar Industrial Ltd., Bangor, County Down, Northern Ireland) (sample code PE).

Method of Exposure, Rinsing, and Leaching

Fifty-centimeter pieces of brand-new construction materials were rinsed with 200 mL of demineralized water to remove soil and residue left during manufacture. The tubing pieces were filled with cleaning solution for 15 min and then inverted to drain the liquid. Laminar flow rinsing (one-way) was carried out by means of different amounts of ultra-pure demineralized water (<0.5 μS/cm); the flow of rinse water was significantly below 5 cm/s at all times. With higher volumes of rinse water,

Table 1. Amount of rinse water (after exposure to cleaning agent, before leaching) used for each sample code

Sample code[a]	Rinse water (mL/m of tubing[b])	Notes
PE, ST 1	0	Not rinsed
PE, ST 2	10	
PE, ST 3	38	Approximate volume of tubing; minimum amount specified[c]
PE, ST 4	200	
PE, ST 5	1,000	Maximum amount specified[c]
PE, ST 6	NA[d]	New tubing, without any contact to cleaning agent (leaching only)

[a] PE = polyethylene tubing. ST = stainless steel coil.
[b] Tubing with a 7-mm inside diameter.
[c] Specified by the cleaning agent manufacturer.
[d] Not applicable.

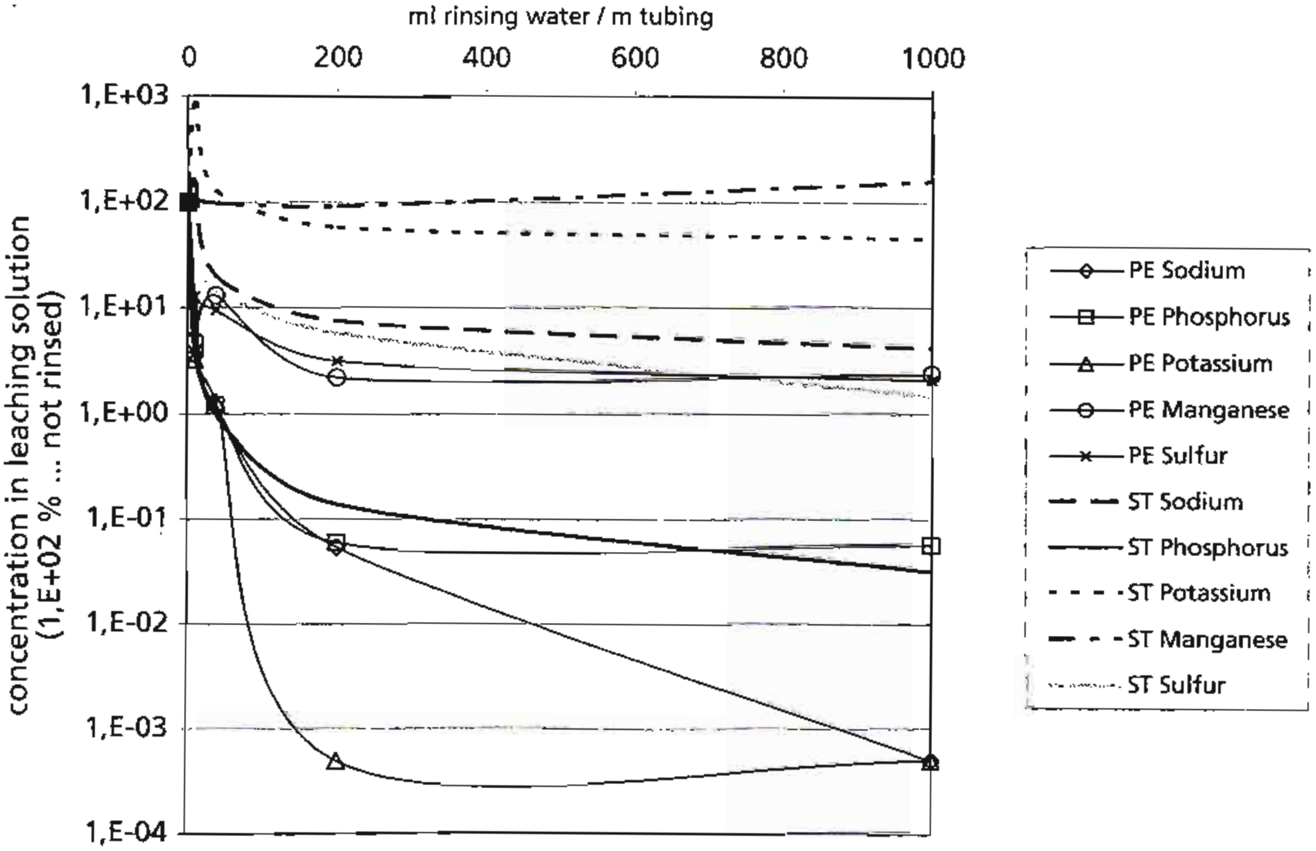

Figure 1. Leaching test results for polyethylene (PE) and stainless steel (ST) tubing.

the tubing was filled completely throughout the rinsing process: with smaller volumes (e.g., 10 and 38 mL/m of tubing), an optimized contact of the liquid with the walls was achieved by rotating the tubing manually during the rinsing process. The tubing was again inverted to drain the excess water.

The leaching solution consisted of 0.05 mole of acetic acid per L of ultra-pure demineralized water, adjusted to a pH of 2.7 to 2.9 with reagent grade carbon dioxide. The leaching solution was chosen to act as a neutralizing medium for the alkaline cleaner and to simulate the properties of a typical beverage (e.g., beer and sparkling soft drinks) with respect to the mobilization potential toward inorganic residue left by the cleaning agent. The pieces of tubing were filled with leaching solution for 60 s (Table 1).

Quantitative Analysis of the Leaching Solutions

Analysis of sodium (^{23}Na), potassium (^{39}K), phosphorus (^{31}P), and manganese (^{55}Mn) was carried out by inductively coupled plasma mass spectrometry (ICP-MS) (ICP-quadrupole mass spectrometer, Perkin-Elmer ELAN 6100; Perkin-Elmer Corp., Wellesley, MA) without any further treatment of the aqueous samples.

Analysis of peroxodisulfate ions was carried out by anion exchange liquid chromatography (high-performance liquid chromatography [HPLC], sodium carbonate mobile phase with a suppressor column and conductivity detection). Peroxodisulfate was quantified from the resulting sulfate anions (after 7 days of reducing action in the acidic, organic leaching solution).

At the time of chromatographic analysis, two of the high-content samples were tested for the absence of peroxodisulfate by the colorimetric ferrous sulfate–thiocyanate method: iron II is spontaneously oxidized by persulfates at pH 2 (sulfuric acid), the resulting iron III ions react with potassium thiocyanate giving a brownish red iron thiocyanate (III), measured photometrically at 470 nm.

Electron Beam Microanalysis (EBMA)

Five-centimeter pieces of the treated polyethylene and stainless steel samples were cut off before the leaching procedure and parts of the inner surfaces were analyzed with a CAMECA SX-100 electron beam microanalyzer (Cameca, Courbevoie Cedex, France) in the energy-dispersive operation mode. To obtain an electrically conductive surface, the polyethylene samples were vacuum-coated with graphite prior to analysis.

Results

Trace Analysis of the Leaching Solution

The analytical data show the different rinsing properties of the polyethylene and stainless steel surfaces. The logarithmic

Table 2. Results of rinsing tests and blank values of untreated construction materials

Sample code[a]	Rinse water (mL/m of tubing)	Sodium (as Na) (mg/L)	Phosphorus (as P_2O_5) (mg/L)	Potassium (as K) (mg/L)	Manganese (as $KMnO_4$) (mg/L)	Sulfur (as $Na_2S_2O_8$) (mg/L)
PE 5[b]	1,000	<0.001	0.005	<0.001	0.003	0.07
PE 6[b]	None[c]	0.56	0.21	0.18	<0.001	0.11
ST 5[b]	1,000	0.08	0.005	0.04	0.96	0.37
ST 6[b]	None[c]	0.12	0.002	0.05	0.99	0.37
PE 4[b]	200	0.01	0.005	<0.001	0.003	0.11
ST 4[b]	200	0.15	0.014	0.06	0.59	0.37
Draft beer[d]	NA[e]	9–230		100–780	<0.6 to 1.0	

[a] PE = polyethylene tubing. ST = stainless steel coil.
[b] In leaching solution.
[c] New tubing, no contact with cleaning agent.
[d] Typical values from literature (6).
[e] Not applicable.

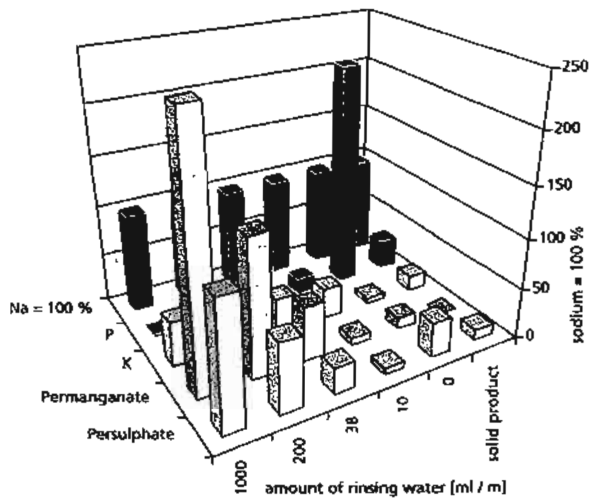

Figure 2. Ratio of different chemical compounds left by the cleaning agent (with respect to sodium at 100%) in the leaching solution of the stainless steel samples (ST).

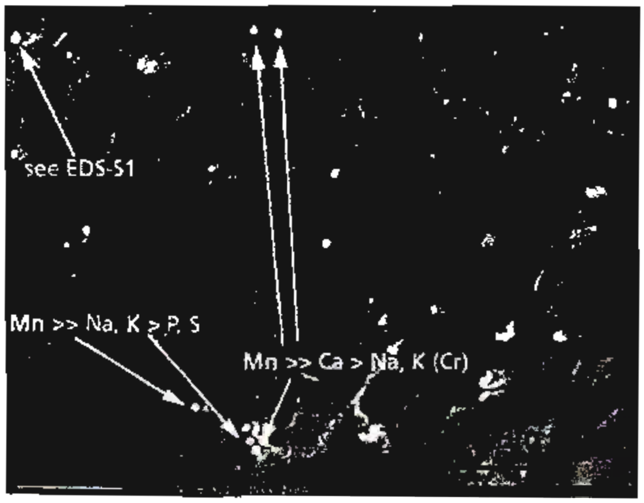

Figure 3. Stainless steel, not rinsed (sample ST 1): Manganese dioxide + traces of other ions left by the cleaning agent. EDS-S1 = energy-dispersive (X-ray) spectrum of a stainless steel sample.

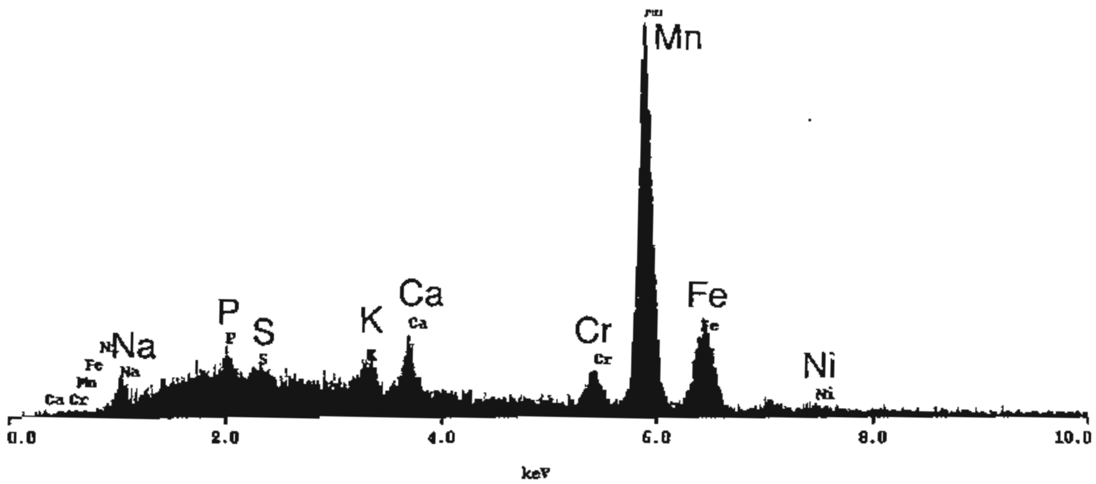

Figure 4. Energy-dispersive analysis from sample ST 1 (stainless steel, not rinsed): EDS-S1 Manganese dioxide.

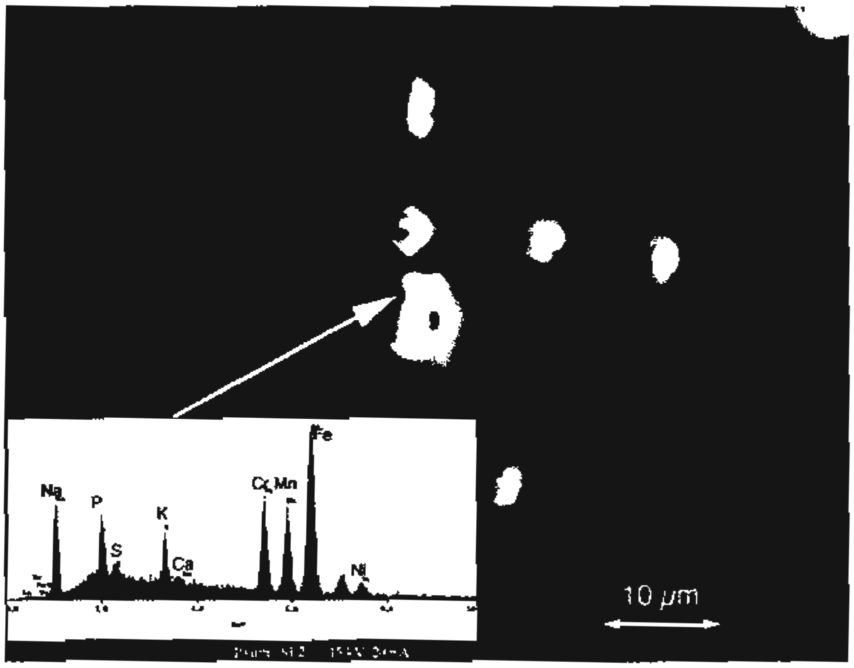

Figure 5. Stainless steel, not rinsed (sample ST 1), detail + energy-dispersive (X-ray) spectrum (EDS) analysis: Residue left by the cleaning agent (Na, P, S, K) with underlying stainless steel.

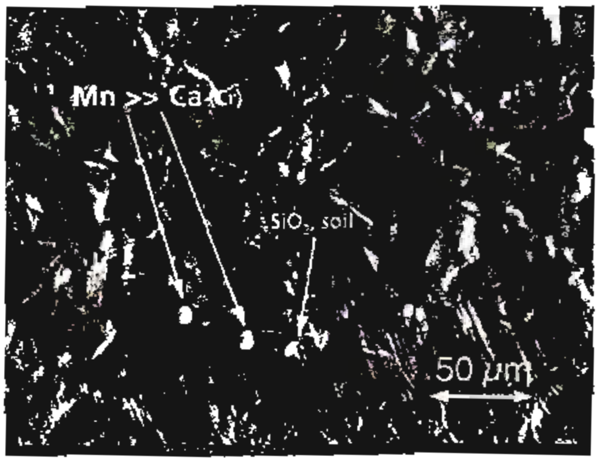

Figure 6. Stainless steel, rinsed (sample ST 4).

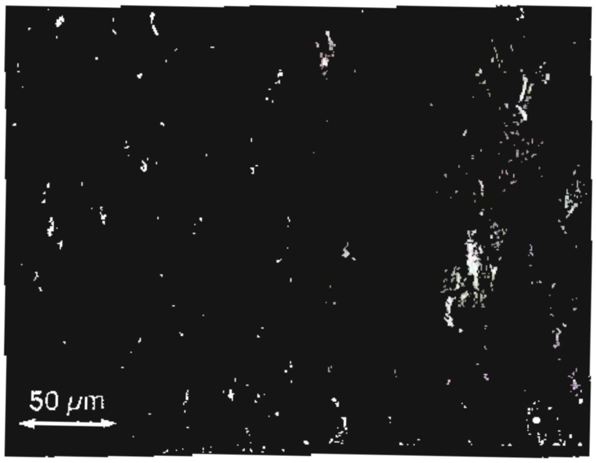

Figure 7. Stainless steel, no contact with cleaning agent (sample ST 6).

plot (Fig. 1) of the concentrations in the leaching solution shows that the rinsing properties of the inert polyethylene surfaces (lines with markers) are far better than those of the stainless steel surfaces (lines only).

The stainless steel rinse data seem to be, in particular, critical for potassium and manganese ions compounds, suggesting that potassium permanganate is retained on the metal surface. If blank concentrations from stainless steel tubing (Table 2, row ST 6) are taken into account, it can be shown that the manganese clearly does not originate from the cleaning agent residue but from the stainless steel itself, which is attacked by the acetic acid/carbon dioxide leaching solution.

Manganese concentrations, being independent of the cleaning procedure (stainless steel samples), suggest that manganese ions can be leached from the stainless steel surface by the beverage passing through the installation. Typical manganese values for draft beer coincide with the analytical results from the acetic acid/carbon dioxide leaching solution (6). Since beer is also in contact with chromium steel from production to dispensing, this leaching phenomena could have an influence on its considerable manganese content.

When 200 mL of rinse water per m of tubing was used, the concentrations of all chemical compounds analyzed (except Mn and K from the stainless steel samples) dropped below 3% (PE) or 15% (ST) of the initial content (no rinsing). This amount of rinse water lies in between the minimum and maximum amount suggested by the cleaning agent manufacturer (5). Additionally, the rinsing properties were different for all other chemical compounds, leading to residuals with a composition different from the original cleaning agent (Fig. 2).

Persulfate ions are not as easily removed from the metal surface as are the other main components (sodium hydroxide and potassium tripolyphosphate). We need to emphasize again that the manganese data (calculated as permanganate) do not necessarily indicate that the actual permanganate residuals are left by the cleaning agents but that they have been proven to originate, to a large extent, from the 1.4301 steel.

Imaging and Semiquantitative Analysis (EBMA)

Microanalysis confirmed the results from the leaching tests, especially with regard to potential influences from different surface properties (e.g., smoothness and electrochemical deposition processes) (Figs. 3–10).

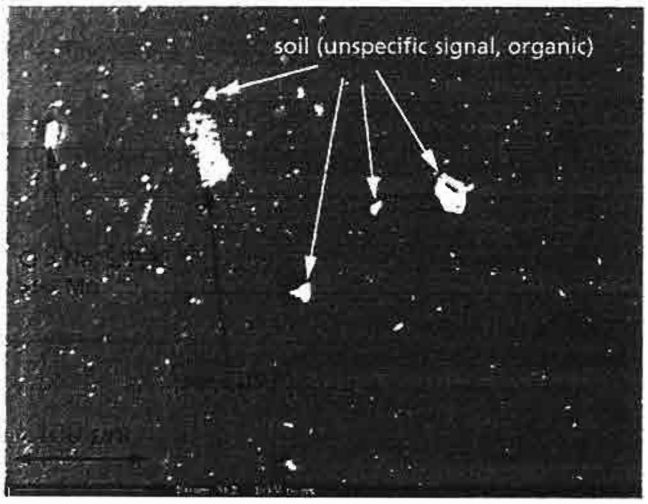

Figure 8. Polyethylene, not rinsed (sample PE 1). EDS-P1 = energy-dispersive (X-ray) spectrum of a polyethylene sample.

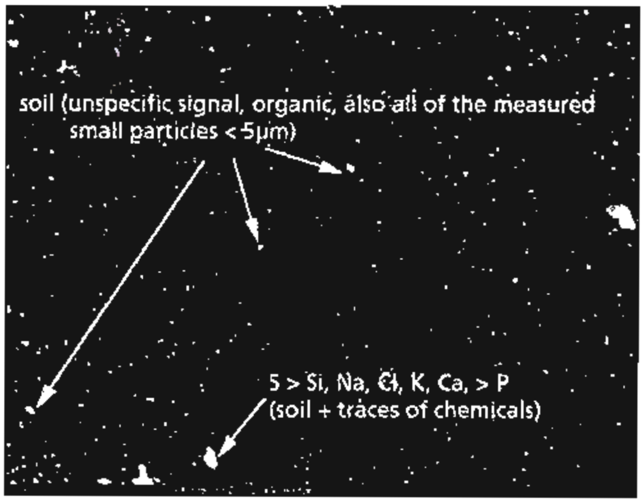

Figure 10. Polyethylene, rinsed (sample PE 4).

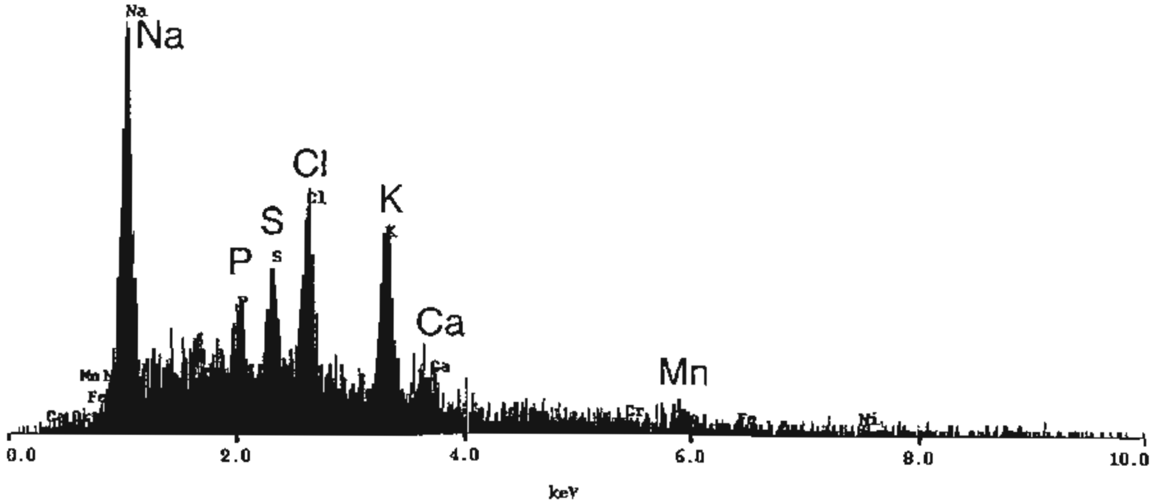

Figure 9. Energy-dispersive analysis from sample PE 1 (polyethylene, not rinsed): EDS-P1 Residue left by the cleaning agent (Na, P, S, K).

Discussion

Comparison with Drinking Water Limit Concentrations

Determining the proper amount of rinse water to use depends greatly on the acceptable limit concentrations for the residuals in the beverage (since analytical results below the actual detection limit cannot be expected when using modern trace methods such as ICP-MS). Because there is little to no actual literature data or regulatory limits on this issue, in particular, for inorganic components, other guideline values need to be considered. If WHO (2) or national (1) drinking water limits or recommended concentrations were available (e.g., manganese, phosphate, sulfate, and sodium), these values were compared with the measured concentrations in the leaching solution (Fig. 11, for sodium persulfate). This comparison is a worst-case-scenario approach, since the test installation is only filled once with the beverage and no portion of the contaminated beverage is withdrawn. In addition, the available LD_{50} (oral, rat) values

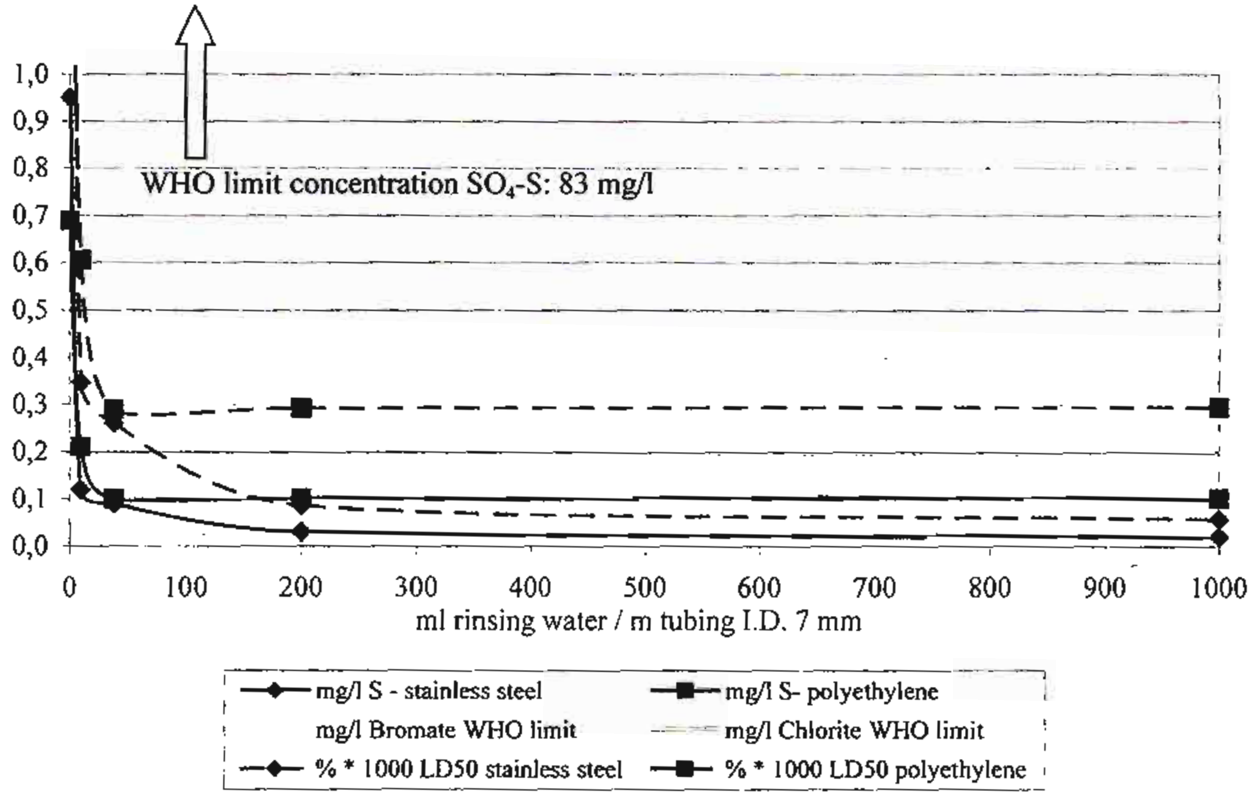

Figure 11. Sulfur compound—sodium persulfate residue.

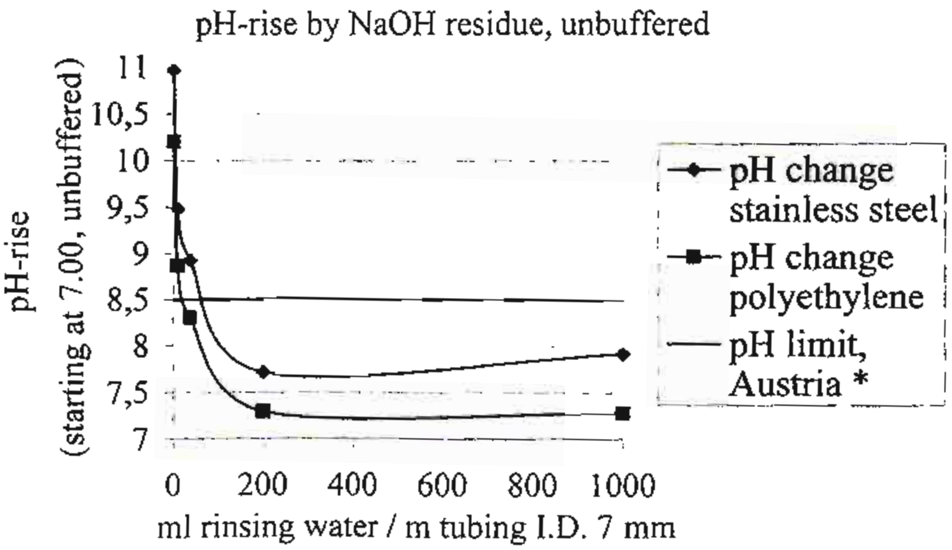

Figure 12. Sodium hydroxide residue and resulting pH. * According to the Austrian federal government (1).

Table 3. Comparison of concentrations in the leaching solution with limit concentrations

Substance	WHO drinking water limit concentration[a] (mg/L)	pH limit[b]	LD_{50}[c] (mg/kg of body weight)	Comparison: substance 1[d]/ WHO limit[a]	Comparison: substance 2[e]/ WHO limit[a]	Rinsing results[f]: Below WHO limit (mL/m)[g]	Below pH limit[h]	Below 0.001% of LD_{50}[i] (mL/m)[g]	Below WHO bromate[j] limit (mL/m)	Below WHO chlorite[k] limit (mL/m)
Sodium		6.5–8.5				0	200			
(as NaOH)						0	38			
Potassium	17[b]					0				
(as KOH)						0				
Phosphorus	0.5[b]		900			38		0		
(as $Na_5P_3O_{10}$)						38		0		
Sulfur	10		920	0.05	0.5	0		0	200	10
(as $Na_2S_2O_8$)						0		0	200	10
Manganese	0		1,090	0.05		...[l]		...[l]	...[l]	
(as $KMnO_4$)						0		0	10	

[a] According to the World Health Organization (WHO) (2).
[b] According to the Austrian federal government (1).
[c] Dose that is lethal to 50% of test subjects (LD_{50}) (oral, rat) (4).
[d] Substance 1 = $NaBrO_3$.
[e] Substance 2 = $NaClO_2$.
[f] Value on top: stainless steel (ST). Value on bottom: polyethylene tubing (PE).
[g] The mL/m value at which point the concentration is below the indicated limit concentration.
[h] Initial pH of 7.00, unbuffered.
[i] Assuming a 70-kg individual and a 0.5-L consumption of the contaminated beverage.
[j] Bromate (BrO_3^-): Carcinogenic inorganic oxidizer.
[k] Chlorite (ClO_2^-): Toxic inorganic oxidizer.
[l] Not applicable, since manganese is mobilized from stainless steel.

(4) for the components of the disinfection cleaner were included, assuming a 70-kg individual and a 0.5-L consumption of the contaminated beverage. The calculated data express the percentage of the LD_{50} uptake reached. For sodium hydroxide residue (calculated from the molar difference of cNa – cS), a theoretical pH increase—starting from pH 7.00—in an unbuffered aqueous solution is displayed (Fig. 12).

Conclusions

The suggested amounts of rinse water (according to application information from the cleaning agent manufacturer) seem to be appropriate (minimum recommended: 38 mL/m of tubing; maximum recommended: 1,000 mL/m of tubing). All of the comparison data (Table 3) show close-to-complete removal of all residue with rinse water volumes from 0 to 200 mL/m of 7-mm-inside-diameter tubing, both from stainless steel and polyethylene surfaces.

Because of a lack of regulatory data, the two potentially hazardous components (potassium permanganate and sodium peroxodisulfate) were compared with two other inorganic oxidizers, known as toxic (chlorite) and carcinogenic (bromate) as follows. With rinse water at 200 mL/m, concentrations in the leaching solution for permanganate, as well as persulfate, drop below the restrictive limit for bromate (1) (0.05 mg/L, as sodium bromate).

The theoretical pH increase of alkali residue showed a similar tendency, leading to pH values below the Austrian limit (4) of pH 8.5 at 38 (PE) and 200 (ST) mL of rinse water per m of tubing (unbuffered, demineralized water with initial pH of 7.00).

It can be concluded that the specified amounts of rinse water (5) are sufficient to achieve a not-detectable-to-insignificant carryover of cleaning agent residues into the dispensed beverage.

ACKNOWLEDGMENTS

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