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Determination of cadmium, lead and thallium in highly saline hemodialysis solutions by potentiometric stripping analysis (PSA)

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Abstract

Potentiometric stripping analysis (PSA) was investigated to assay simultaneously cadmium, lead and thallium present as contaminants in highly saline solutions used in hemodialysis. The saline matrices were sodium, potassium, magnesium and calcium chlorides, sodium acetate, sodium bicarbonate and glucose, which constitute concentrates for hemodialysis. A 1000 $\mu g\,mL^{-1}$ Hg(II) solution was used to prepare the mercury film electrode (MFE) and to carry out the stripping step. After a 30 s accumulation interval the analytes were simultaneously detected in the saline matrices without using masking agents. Determination limits of 80 $ng\,L^{-1}$ for cadmium and thallium, and 50 $ng\,L^{-1}$ for lead were calculated and a R.S.D. ranging from 0.5 to 2.2% (n = 3) was obtained measuring the analytes directly in commercial hemodialysis saline solutions. Recoveries from spiked samples ranging from 94.6 to 102.0% were obtained. The investigated metals were found in concentrations ranging from 2.7 to 5.7 $\mu g\,L^{-1}$ for cadmium, 27.7 to 75.8 $\mu\,L^{-1}$ for lead and 9.6 to 18.7 $\mu g\,L^{-1}$ for thallium in commercial hemodialysis solutions. The PSA method showed to be adequate to the quality control of saline concentrates for hemodialysis.

Keywords: Potentiometric stripping analysis; Mercury film electrode; Hg(II) oxidant solution

1. Introduction

Renal patients are subject to some trace element disturbances during hemodialysis treatment that might occur due to the transference of contaminants from the dialysis fluid (DF) to the blood of the patients [1–3]. The main source of dialysate trace metal contamination is frequently ascribed to tap water, but the highly saline (HS) solutions that are mixed to the hemodialysis water to compose the DF, may also contribute to increase the concentration of a number of unwanted trace metals. The oral intake of some metallic species present as contaminants in foodstuff and drinking water must be avoided even for people with normal renal function since full elimination through the excretory system is rarely reached. Chronic contamination can be observed in these cases when the metallic species are continuously accumulated in some body parts as bones [4], liver [5] and brain [6]. The WHO recommends to the quality control of hemodialysis solutions that toxic metallic species need to be detected at low concentration levels only in the water used to prepare the DF solutions. On the other hand, for HS solutions there are only recommendations to use high purity starting material to prepare it. Additionally, it is well known that some contaminants are also present in products labelled as high purity materials. Concerning to the chlorides of magnesium, calcium, sodium and potassium, that are the main starting material for the HS solutions, cadmium, lead and thallium are frequently indicated as contaminants by the suppliers. For example, KCl and NaCl labelled by Merck as Suprapur grade should contain no more than 0.1 ppm cadmium, lead and thallium and for these salts labelled as AR grade the tolerable limit is still higher (ca. 0.001%). Although the main part of trace metal related problems in dialysis patients are attributed to the toxic

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effects of aluminium [1–3,7], a number of other elements can also be dangerous to the health of patients.

There is no reference materials for hemodialysis HS solutions and their saline concentrations seriously restrict the amount of available methods although the electrothermal atomic absorption spectrometry (ETAAS) has been used as the current analytical technique for metallic trace determinations in water and DF solutions [8–10]. However, it fails to assay directly trace metals in the HS solutions because either metallic contaminants are close to the limits of determination of linesource ETAAS or the precision is not sufficient in these media. The saline concentration in the HS solutions is about of 400 g L^{-1}, essentially chlorides of sodium, potassium, magnesium and calcium so that, even modern AAS instruments, including the Zeeman background correction system or transversely heated graphite atomizer, do not overcome the problems associated with the high saline content of the solutions. The usual practice of diluting samples also do not solve the problems in these matrices. Alternatively, clean up/preconcentration procedures using conventional ion exchangers and sorbents like modified silica gels [11] and more recently polyethylene powder [12] can be used to overcome the matrix interference, however, these procedures are always time consuming and frequently experienced analysts are required to conduct the analysis.

Electrochemical methods like potentiometry and voltammetry show as general characteristics for metal trace analysis low interference levels by saline matrices and high detection sensitivities mainly in the so-called "built-in" preconcentration methods [13–18]. In this work, stripping potentiometry was investigated to detect simultaneously very low concentrations of cadmium, lead and thallium present as contaminants in hemodialysis HS solutions. The target was to develop a sensitive, easy and not expensive method to be used for commercial hemodialysis HS samples skipping prior treatments to overcome matrix interferences.

2. Experimental

2.1. Instrumentation and apparatus

Potentiometric analyses were carried out by using a PSA ION 3 potentiometric stripping analyzer (Steroglass, S. Martino in Campo, Perugia, Italy), connected to an IBM-compatible personal computer. A 40 mL cell was used with a three-electrode system consisting of a 3 mm diameter working glassy carbon electrode (GCE), a platinum wire counter electrode and a silver/silver chloride/saturated potassium chloride reference electrode (Steroglass). All electrochemical measurements were made under stirring during the plating and electrolysis (accumulation) steps. During the stripping step the solutions were maintained under quiescent conditions. The analyzer operates under the control of the NEOTES 2.0 software package (Steroglass).

Stripping voltammetry was used as comparative method and the measurements were made on a Metrohm 646 VA Processor/675 VA Sample Changer operating at the HMDE (hanging mercury electrode) mode measurement with a platinum wire as counter electrode. The voltammograms were recorded in the potential range between −900 and −100 mV. All potentials quoted were measured against an Ag/AgCl, KCl 3 mol L^{-1} reference electrode and the cell volume was 20 mL.

2.2. Reagents and solutions

All chemicals were of analytical-reagent grade. All aqueous solutions were prepared with distilled and deionized water, that was further purified by a Milli-Q high purity water device (Millipore, Bedford, USA). The metals stock standard solutions containing 1000 mg L^{-1} were prepared from $Cd(NO_3)_2{\cdot}4H_2O$, $Pb(NO_3)_2$ (Merck, Darmstadt, Germany) and $TlNO_3$ (Sigma, St. Louis, USA) and working standard solutions by suitable dilutions of the stock solutions.

The commercial HS solutions had the following composition – concentrate I: Solurin (JP Indústrias Farmacêuticas, São Paulo, Brazil) with 684.82 g NaCl; 598.94 g CH_3COONa; 18.06 g $MgCl_2$, 22.20 g $CaCl_2$ and 300.20 g of glucose in 3.6 L; concentrate II: HB 120 L (Salbego, São Paulo, Brazil) with 864.40 g NaCl; 13.41 g KCl; 6.27 g $MgCl_2$, 23.10 g $CaCl_2$ and 108.00 g of glucose in 3.4 L; concentrate III: HB Bic (Salbego) with 947.6 g NaCl; 18.0 g KCl; 12.4 g $MgCl_2$, 46.8 g $CaCl_2$ and 352.8 g of $NaHCO_3$ in 4.0 L; concentrate IV: HD 3,5 (B. Braun, São Paulo, Brazil) with 864.40 g NaCl; 13.41 g KCl; 6.27 g $MgCl_2$, 23.10 g $CaCl_2$, 352.8 g $NaHCO_3$ and 108.00 g of glucose in 3.4 L. Artificial HS solutions were prepared following the composition of the concentrate III HB Bic (Salbego) by using AR grade reagents as starting material (Merck).

2.3. Plating

Before starting a set of analyses, the GCE was gentle polished with a wet filter paper and well cleaned with absolute methanol, Milli-Q high purity water, diluted nitric acid (1%, v/v) and again with the Milli-Q water. A mercury film was then plated in situ onto the GCE by putting in the electrochemical cell 20 mL of the plating solution (1000 μg mL^{-1} Hg(II) nitrate solution in 1.0 mol L^{-1} ultrapure hydrochloric acid solution) and carrying out the electrolysis at −900 mV, against the reference electrode, for 60 s. During this step the solution was stirred by the PSA ION 3 glass stirrer choosing the speed 7 (1200 rpm) on the NEOTES 2.0 software. After the plating, the Hg(II) solution was stored in a plastic bottle to rebuild the MFE when necessary.

2.4. Potentiometric determinations

The determination of cadmium, lead and thallium was carried out by adding to the electrochemical cell 20 mL of the

sample (hemodialysis HS solution) and 500 μL of the plating solution in order to have Hg(II) as oxidant to the stripping step and to maintain the pH in the interval 0.5–1.0. Every analysis was conducted in tree cycles, utilizing the multiple standard addition method by adding at the end of every cycle the suitable volume (10–100 μL) of cadmium, lead and thallium (0.1–30 mg L^{-1}) standards. The peak area was plotted against standard concentration, obtaining a calibration straight. The potential range used was −900 to − 300 mV and the plating potential −900 mV.

2.5. Voltammetric determinations

The analytes were determined by anodic stripping voltammetry (ASV) by putting 20 mL of the hemodialysis HS solution in the cell, 10 μL of concentrated $HClO_4$ and solid EDTA in order to have a concentration of 0.01 mol L^{-1} in the cell when was necessary to mask lead ions to detect thallium. For all measurements the differential pulse mode was used. Voltammograms were recorded between −900 to −300 mV with a scan rate of 10 mV s^{-1}, a pulse amplitude of 50 mV and a pulse duration of 40 ms.

3. Results and discussion

For renal patients the risk to develop a chronic contamination from a long-term poisoning (even at trace levels) is considerably higher than for healthy people as the renal patients can not eliminate the toxic species in consequence of the inadequate renal function. The presence of contaminants in potable water or in HS solutions must be detected before the hemodialysis sessions as the DF solution remains very close to the blood of the patients separated from it only by the dialysis membranes. To aggravate the problem, the dialysis membranes can dialysate many toxic substances as hemodialysis is frequently the procedure adopted in the treatment of patients with acute intoxication symptoms [19–22].

3.1. Determination of cadmium, lead and thallium by PSA in HS solutions

The potentiometric method was initially tested in aqueous solutions containing the analytes and not containing the salts used in the HS formulations. Fig. 1a shows a representative stripping potentiogram obtained after the addition of 10 μL (curve 1) and 30 μL (curve 2) of a 10 mg L^{-1} standard of cadmium, lead and thallium to the electrochemical cell containing only 19.5 mL pure water and 500 μL of the Hg(II) oxidant solution. The potentiograms shows a combined response for cadmium and thallium in the potential range of −720 to −500 mV, so that a masking agent was necessary to assay simultaneously cadmium, lead and thallium in aqueous solutions not containing high saline levels. However, changes in the peak potentials were observed in presence of the HS solution. For increasing amounts of HS

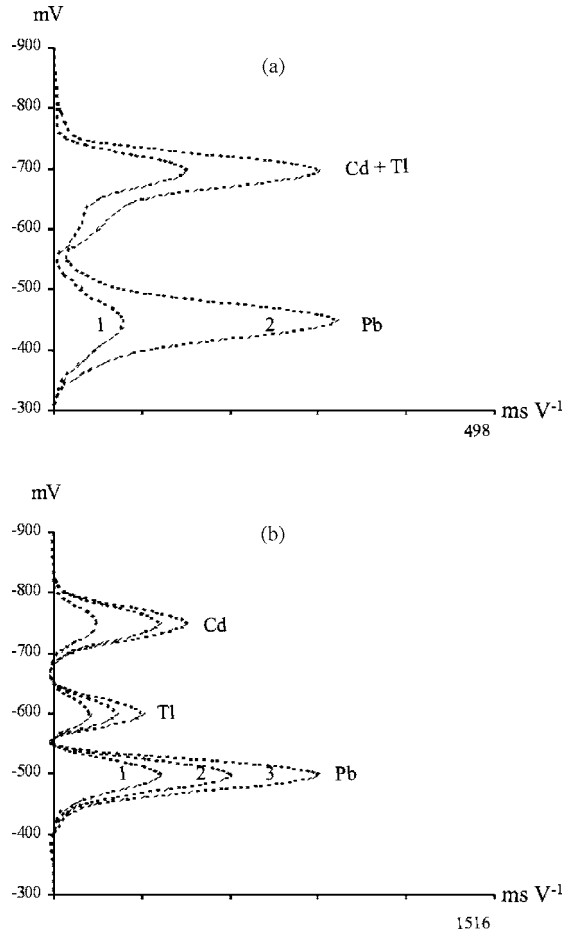

Fig. 1. Stripping potentiograms utilizing the multiple standard addition method. (a) In the potentiometric cell 20 mL pure water and 500 μL Hg(II) oxidant solution. Curve 1, 50 ng and curve 2, 150 ng Cd(II), Pb(II) and Tl(I). (b) In the potentiometric cell 20 mL hemodialysis HS sample and 500 μL Hg(II) oxidant solution. Curve 1, HS sample; curve 2, HS sample and 200 ng Cd(II), 400 ng Pb(II), 300 ng Tl(I); curve 3, HS sample and 400 ng Cd(II), 800 ng Pb(II), 600 ng Tl(I). Accumulation time 30 s.

solutions in the electrochemical cell, the cadmium and thallium peaks turned gradually into two separate peaks, so that for ratios between HS solution and water starting from 5:15 (v/v) they kept well resolved. Fig. 1b shows the peak profiles obtained by assaying the analytes in a commercial HS sample where only the sample (20 mL) and the oxidant solution (500 μL) were added to the electrochemical cell (curve 1). The peaks of cadmium, lead and thallium are well separated in the potential window of −800 to −300 mV. After the addition of two 20 μL aliquots of a standard 20.0 mg L^{-1} Pb(II), 15.0 mg L^{-1} Tl(I) and 10.0 mg L^{-1} Cd(II), the curves 2, 3 (Fig. 1b) were obtained. Concentrations of 5.0, 25.3 and 11.3 μg L^{-1} in the HS sample were calculated by regression for cadmium, lead and thallium, respectively. The accumulation time was 30 s and peak area was used to calculate the analyte concentrations.

The well resolved stripping peaks observed for cadmium, lead and thallium in HS solutions and not in pure water can be attributed to the combined action of two different effects. A

potential shift to negative values caused by the chloride ions owing to metal chloro-complexes formation and a potential shift to positive values caused by the high IS existing in HS solutions. Indeed, thallium that forms the weakest chloro-complex ($\log k = 0.52$) [23] in comparison to cadmium ($\log k = 2.05$) [23] and lead ($\log k = 1.62$) [23] showed the least pronounced negative potential shift in the HS solutions. In contrast, the very high saline concentration in HS solutions decreases the hydratation number of the metallic species and shift their reduction potential to positive values. These shifts for aquo ions exhibit a pattern of increasing anodic potential shift with increasing charge and hydratation number [24], so it was less pronounced for thallium in comparison to cadmium and lead. Hence, the observed separations of the three peaks can be explained by both effects acting simultaneously in different extensions for each metallic species. It is also important to point out that to detect very low analyte concentrations by PSA, very short transition times must be used so that a sampling time of 300 μs was necessary in this work to detect analyte concentrations of few $\mu g\,L^{-1}$ or even lower. Due to the high chloride concentrations in HS samples, a special care was necessary during the determinations. The potential was never let to reach values more positive than 0.0 V to avoid calomel formation and electrode deterioration.

3.2. Analytical characteristics of the PSA method

The criteria 10σ and 3σ (n =5) [25] were used here to calculate limits of determination and detection, respectively. It is well known that for built-in preconcentration methods, the calculated limits depend in some extension on the accumulation time used, therefore determination limits of 80 $ng\,L^{-1}$ for cadmium and thallium, and 50 $ng\,L^{-1}$ for lead could be calculated by using a 120 s accumulation interval.

Linear calibration graphs were obtained for cadmium, lead and thallium assayed individually by PSA in pure water. Table 1 shows the calibration parameters and also the normalized slopes of the calibration curves in order to set up a relationship between accumulation time and sensitivity. Although longer accumulation intervals were associated to higher slopes of the calibration curves, lower ratios between the slopes were observed for intervals higher than 30 s, so that despite the improvement on the sensitivity, accumulation intervals higher than 30 s were not interesting from the point of view of the analysis duration. The relationships amongst normalized slopes and accumulation times were roughly linear ($R^2 = 0.89$) but even so at each accumulation time good linear fits ($R^2 > 0.98$) were obtained between concentration and analytical signal. Although the determinations of each analyte individually by PSA have showed similar results in pure water and in artificial HS solutions, the analytical characteristics of the PSA method were investigated only in pure water because it is difficult to obtain good blanks even with artificial HS solutions since the starting products are always previously contaminated in some extension by cadmium, lead or thallium.

Table 1
Characteristics of the calibration graphs for cadmium, lead and thallium in pure water by PSA

Analyte	Accumulation time (s)	Range of linearity ($\mu g\,L^{-1}$)	r	Slope[a] ($ms\,V^{-1}\,L\,\mu g^{-1}$)
Cd	10	10.0–200.0	0.998	0.69
Pb	10	5.0–200.0	0.999	0.59
Tl	10	10.0–200.0	0.995	0.47
Cd	30	0.10–120.0	0.999	0.84
Pb	30	0.08–120.0	0.999	0.77
Tl	30	0.10–120.0	0.999	0.68
Cd	60	0.10–100.0	0.997	0.92
Pb	60	0.08–100.0	0.995	0.89
Tl	60	0.10–100.0	0.998	0.84
Cd	90	0.10–100.0	0.996	0.97
Pb	90	0.08–100.0	0.998	0.96
Tl	90	0.10–100.0	0.995	0.94
Cd	120	0.10–100.0	0.993	1.00
Pb	120	0.08–100.0	0.997	1.00
Tl	120	0.10–100.0	0.995	1.00

[a] Normalized values.

3.3. Determination of cadmium, lead and thallium by PSA in HS solutions

Recovery experiments are more properly used when during the determinations or sample treatment, additional steps that can influence the change of the analyte concentration are introduced. Although it was not the case in this work since the analytes were assayed in acidic media, recovery experiments were adopted here because glucose, which shows reducing properties, was present in considerable concentrations in the commercial HS samples. Table 2 shows the detected concentrations and also the recoveries from spiked commercial HS samples. Thallium was found in all samples probably because it is a common contaminant of the alkaline metals present in the HS solutions due to the similarity amongst their ionic radii [26]. Lead was the prevalent contaminant in opposition to cadmium that was found only in very low concentrations.

3.4. Interferences from electroactive species in PSA method

Iron(III), zinc(II) and Cu(II) were tested as metallic interfering species because they can also be present as contaminants of the main salts used to produce the HS solutions. As could be expected no interference were observed by the presence of these ions. Iron(III) is not reduced to elemental iron at a mercury electrode, unless the accumulation step is set at potentials cathodic of about −1350 mV (versus Ag/AgCl sat.), hence no stripping signals from iron appeared for the accumulation potential used in this work. Similarly, zinc(II) is also reduced at a mercury electrode at accumulation potentials cathodic of about −1000 mV (versus Ag/AgCl sat.) so that keeping the accumulation potential by −900 mV (versus Ag/AgCl sat.), zinc(II) species were not deposited on the GCE and the possible interference from intermetallic Zn/Cu species was avoided.

Table 2
Determination and recovery for cadmium, lead and thallium in commercial HS solutions by PSA

HS sample[a]	Added			Detected			Recovery		
	Cd ($\mu g\,L^{-1}$)	Pb ($\mu g\,L^{-1}$)	Tl ($\mu g\,L^{-1}$)	Cd ($\mu g\,L^{-1}$)	Pb ($\mu g\,L^{-1}$)	Tl ($\mu g\,L^{-1}$)	Cd (%)	Pb (%)	Tl (%)
A	0.0	0.0	0.0	4.0	35.3	9.7	–	–	–
	25.0	25.0	25.0	28.2	60.8	33.9	97.2	100.8	97.7
B	0.0	0.0	0.0	2.7	27.7	14.4	–	–	–
	25.0	25.0	25.0	26.9	51.9	38.7	97.1	98.5	98.2
C	0.0	0.0	0.0	4.9	28.6	12.6	–	–	–
	25.0	25.0	25.0	29.2	52.7	37.3	97.6	100.0	94.6
D	0.0	0.0	0.0	4.3	49.3	18.7	–	–	–
	25.0	25.0	25.0	29.8	75.8	42.9	101.7	102.0	98.2
E	0.0	0.0	0.0	5.7	45.4	18.3	–	–	–
	25.0	25.0	25.0	31.2	71.2	43.8	101.6	101.1	101.1

[a] HS solutions: JP (Solurin); Salbego (HB and HB Bic); Braun (HD); R.S.D. ranged from 0.5 to 2.2% (n = 3).

3.5. Determination of cadmium, lead and thallium by ASV in HS solutions

Since there is no reference material for HS solutions, we used the recovery experiments displayed in Table 2 to validate the data. Additionally, ASV with the HMDE as working electrode was also used to assay the analytes in artificial HS samples, since determinations of cadmium, lead and thallium are well documented by voltammetry in many samples [27–31]. In order to compare the methods, 13 artificial hemodialysis HS samples spiked with the analytes (concentrations up to 140.0 $\mu g\,L^{-1}$) were assayed by PSA and ASV methods. The mutual interference between lead and thallium observed by ASV was avoided by adding to the voltammetric cell EDTA [16,32] as thallium build no stable complex with this masking agent. Preliminary studies showed a decrease in the sensitivity of the ASV method when glucose concentrations in HS solutions were 40 $g\,L^{-1}$ or higher (the normal value in HS formulations is ca. 80 $g\,L^{-1}$). This way, glucose was not added to the artificial HS samples but all other constituents that compose the HB Bic samples (see Section 2) were included. Although both methods have similar built-in accumulation steps, they showed in HS solutions different stripping steps. The best signal discrimination obtained by PSA in comparison with ASV can be ascribed to the association of two main aspects; the used working electrodes (MFE in PSA and HMDE in ASV) and the chemical oxidation in PSA instead of electrochemical oxidation in ASV during the stripping steps. Indeed, the self-optimized potential scan-rate obtained by PSA during the stripping step by the action of the oxidant [33] associated with the highest resolving power of the MFE [34] was in benefit of a best signal discrimination by the PSA method. Additionally, the different overpotential of the thallium ions for their redox reactions at MFE and HMDE [35] was also in favor of a superior signal discrimination by the PSA method. In short, to assay cadmium, lead and thallium in HS solutions only by PSA, the glucose elimination and the addition of masking agent (EDTA) was not necessary to obtain well-separated signals.

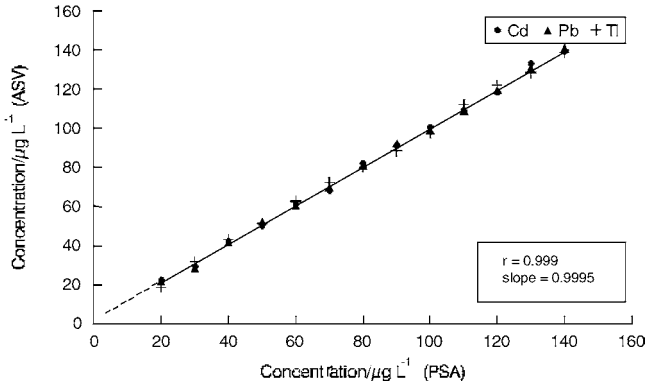

Fig. 2. Regression analysis of cadmium, lead and thallium determined by PSA and ASV methods in artificial HS samples without glucose. Preconcentration time 30 s.

The regression analysis displayed in Fig. 2 indicates that the methods produced similar results, although the voltammetric method was more time consuming due to the necessity of repeating the measurement after adding the masking agent. Otherwise, according to the used conditions, concentrations lower than ca. 15 $\mu g\,L^{-1}$ were only detected by the PSA method (dashed line in Fig. 2). The higher sensitivity obtained by the PSA method can be attributed to its less significant background signals as the charge currents are lower by PSA than ASV [33] and because the addition of EDTA was not necessary by PSA. Additionally, a more simple equipment is used in PSA as no potential waveform generator is required [36].

4. Conclusions

The PSA method can be the choice to determine cadmium, lead and thallium as contaminants in the saline solutions used in hemodialysis procedures. The determinations are easy to perform, the selectivity and sensitivity are adequate to control the quality of HS solutions, the instrumental is not expansive

and the analytes were rapidly assayed free of interferences in real samples. Concentrations of the analytes ranging from 2.7 to 5.7 $\mu g\,L^{-1}$ for cadmium, 27.7 to 75.8 μL^{-1} for lead and 9.6 to 18.7 $\mu g\,L^{-1}$ for thallium were determined in commercial HS samples without the necessity to use masking agents or dilute the samples to overcome interferences. Although the concentration of all contaminants was not high in the assayed samples, these values should be considered by HS solutions' suppliers as all the content of these solutions (and not only a sample of it) is used in a hemodialysis session. Additionally, the HS solution remains very close to the blood of the patients that have no normal renal function.

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