Electronic Supplementary Material (ESI) for RSC Advances.

Corrosion process of stainless steel in natural brine as a source of chromium and iron - the need for routine analysis

Supplementary Material

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Table S1. The results of the recovery study regarding Cr. Optimization of the sample preparation procedure was based on the results of UV-Vis determination of Cr in brine spiked with Cr(III) and/or Cr(VI) standard solutions.

Extraction: to extract total chromium, it was first oxidized to Cr(VI) by $KMnO_4$ in the presence of 0.1 mol L^{-1} H_2SO_4. The solution was heated in a boiling water bath (T=100°C). Then, the samples were acidified with HCl to obtain the final concentration of 2 or 3 mol L^{-1}, and 15.0 mL of the sample was placed in a separating funnel. Cr(VI) was extracted with three portions (5.0 mL each) of 4-methyl-2-pentanone at a temperature below 10°C, and next re-extracted with three portions of deionized water (5.0 mL) at room temperature.

Thermal chloride stripping: concentrated H_2SO_4 was added to the sample in an amount that allowed to obtain the final concentration (after evaporation and dilution) within the range of 0.05-0.1 mol L^{-1}. The sample was then heated to approximately 210°C until characteristic white fumes were observed. After cooling and dilution with DI water, $KMnO_4$ solution was added to oxidize chromium to Cr(VI).

Thermal chloride stripping (without $KMnO_4$): the oxidation step with $KMnO_4$ was omitted. In this experiment, the preparation of the samples was limited to chloride stripping with sulphuric acid only.

Sample	Concentration of Cr [µg mL^{-1}]		Recovery [%]
	added	determined	
Preliminary study – no sample preparation			
therapeutic brine (diluted 10x) spiked with Cr(VI)	0.100	0.059	59
	0.100	0.090	90
therapeutic brine (diluted 100x) spiked with Cr(VI)	0.100	0.084	84
	0.100	0.097	97
Extraction			
model brine spiked with Cr(VI), 2 mol L^{-1} HCl	0.500	0.340	68
	0.500	0.381	76
	0.500	0.420	84
	0.500	0.340	68
	0.500	0.340	68
	0.500	0.390	78
model brine spiked with Cr(VI), 3 mol L^{-1} HCl	0.500	0.251	50
model brine spiked with Cr(III), 2 mol L^{-1} HCl	0.500	0.634	127
	0.500	0.629	126
	0.500	0.530	106
	0.500	0.527	105
	0.500	0.496	99
	0.500	0.338	68
	0.500	0.411	82
Thermal chloride stripping			
model brine spiked with Cr(III)	0.500	0.458	92
	0.500	0.338	68
	0.500	0.414	83
	0.500	0.389	78
model brine spiked with Cr(VI)	0.500	0.592	118
	0.500	0.598	120
	0.500	0.592	118
	0.500	0.572	114

Thermal chloride stripping (without $KMnO_4$)			
model brine spiked with Cr(III)	0.500	< LOD	0
	0.500	< LOD	0
	0.500	< LOD	0
model brine spiked with Cr(VI)	0.500	0.015	3
	0.500	0.072	14
	0.500	0.157	31
	0.500	0.189	38

Table S2. The results of the recovery study regarding Fe. Optimization of the sample preparation procedure was based on the results of UV-Vis determination of Fe in water and brine spiked with Fe standard solution.

Iron was extracted from the sample using 4-methyl-2-pentanone (hexone), re-extracted with 0.1 mol L^{-1} HCl and determined using spectrophotometry after addition of sulfosalicylic acid. Standard solutions of Cr(III) and Cr(VI) were added to test the method for interferences. The concentration of each element was 2 mg L^{-1}, and Fe was determined without prior extraction.

Sample	**Concentration of Fe [μg mL^{-1}]**		**Recovery [%]**
	added	**determined**	
DI water spiked with Fe	2.00	1.70	85
	2.00	1.80	90
	2.00	1.84	92
model brine spiked with Fe	2.00	1.87	94
	2.00	1.88	94
	2.00	1.84	92
	2.00	1.85	93
	2.00	1.81	91
	2.00	1.71	86
	2.00	1.80	90
DI water spiked with Fe	2.00	1.91	96
DI water spiked with Fe and Cr(III) 1:1	2.00	1.96	98
DI water spiked with Fe and Cr(VI) 1:1	2.00	2.15	108
model brine spiked with Fe and Cr(VI) 1:1	2.00	1.85	93
	2.00	1.64	82
model brine spiked with Fe and Cr(III) 1:1	2.00	1.85	93
	2.00	1.83	92