

**Supplement 1:** Comparison of calculated and measured chlorine isotopic composition and fraction  $^{37}\text{Cl}$  for natural and enriched  $^{37}\text{Cl}$  solutions shown in Figure 2. Note that the buffer solution reported here started as a mixture of 60 mM KCl, 0.4 mM Orange G, 10 mM EACA titrated to pH 10 using  $\text{NH}_4\text{OH}$ , and 10 mM ammonium thiosulfate titrated to pH 9.29 with  $\text{NH}_4\text{OH}$ .

<b><i>NIST SRM 975a matrix</i></b>							
$^{37}\text{Cl}/^{35}\text{Cl}_{\text{calc}}$	$^{37}\text{Cl}/^{35}\text{Cl}_{\text{meas}}$	$1\sigma$	% diff	Fract. $^{37}\text{Cl}_{\text{calc}}$	Fract. $^{37}\text{Cl}_{\text{meas}}$	$1\sigma$	% diff
0.3197	0.3200	0.0013	0.10%	0.2423	0.2424	0.0010	0.08%
0.4235	0.4246	0.0012	0.26%	0.2975	0.2981	0.0008	0.18%
0.5871	0.5764	0.0020	-1.81%	0.3699	0.3657	0.0012	-1.15%
0.7457	0.7371	0.0056	-1.16%	0.4272	0.4243	0.0032	-0.67%
<b><i>HCl matrix</i></b>							
$^{37}\text{Cl}/^{35}\text{Cl}_{\text{calc}}$	$^{37}\text{Cl}/^{35}\text{Cl}_{\text{meas}}$	$1\sigma$	% diff	Fract. $^{37}\text{Cl}_{\text{calc}}$	Fract. $^{37}\text{Cl}_{\text{meas}}$	$1\sigma$	% diff
0.3197	0.3192	0.0029	-0.14%	0.2423	0.2420	0.0022	-0.11%
0.8611	0.8622	0.0088	0.13%	0.4627	0.4630	0.0047	0.07%
2.3869	2.3916	0.0239	0.20%	0.7047	0.7052	0.0070	0.06%
18.2385	18.2463	0.1424	0.04%	0.9480	0.9480	0.0074	0.00%
52.2466	53.3745	0.5036	2.16%	0.9812	0.9816	0.0093	0.04%
<b><i>Buffer matrix</i></b>							
$^{37}\text{Cl}/^{35}\text{Cl}_{\text{calc}}$	$^{37}\text{Cl}/^{35}\text{Cl}_{\text{meas}}$	$1\sigma$	% diff	Fract. $^{37}\text{Cl}_{\text{calc}}$	Fract. $^{37}\text{Cl}_{\text{meas}}$	$1\sigma$	% diff
0.3197	0.3190	0.0011	-0.21%	0.2423	0.2419	0.0008	-0.16%
0.4241	0.4200	0.0010	-0.96%	0.2978	0.2958	0.0007	-0.68%
0.5826	0.5752	0.0037	-1.26%	0.3681	0.3652	0.0024	-0.80%
0.7431	0.7295	0.0030	-1.82%	0.4263	0.4218	0.0018	-1.05%