

Report on Investigation Into issues with Sediments

Recently a number of samples have been cancelled due to sediment being apparent in "Filtered" sample bottles. This is normally indicative of the sample having been incorrectly filtered or having not been filtered. Following discussion with the client, where it has been confirmed the samples have been filtered appropriately, further investigation has been undertaken to ascertain the cause of this issue

One client sample was chosen, which had visible particulates in the Nitric Preserved Sample. The plastic, unpreserved bottle was removed from the cold store, and allowed to stabilise at room temperature. This was then filtered within the laboratory with a 0.45um syringe filter and acidified to mimic the process occurring in the field. At this point there were no visible sediments. This stage was carried out in duplicate.

The sample was checked the following morning, and there were faint signs of some visible particulates appearing. After a following 24 hours this had become visible sediment. This is shown below in figures 1 – 3.



Fig1: No particulates present



Fig2: 24 Hours, separation visible



Fig3: 48 Hours visible layering

As this was carried out in duplicate, the samples were analysed following two different procedures. One sample was analysed using the routine, validated, dissolved method procedure. This involves further acidification, followed by analysis via ICPMS.

The second sample was analysed using the routine, validated, total metals method. This involves acidification, digestion at 95degC, followed by analysis via ICPMS. This is a more vigorous digestion method to break down particulates found in unfiltered samples that are not present in filtered aliquots. The results of both samples were compared. All results were comparable with the exception of the Chromium where a higher result was observed in the hot digest. Results are below in Table 1.



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Element	LOD	Method Precision (%)	Filtered Digest	Total Digest	Results Consistent
7Li (STD)	3	10	153.00470	157.68890	Yes
9Be (STD)	0.1	10	0.00431	0.00515	Yes
11B (STD)	10	10	1790.15653	1817.21192	Yes
23Na (KED)	76	10	630450.97407	679854.12299	Yes
24Mg (KED)	36	10	40865.12869	41328.31859	Yes
27Al (STD)	10	10	123.90217	132.21968	Yes
31P (KED)	10	10	6060.56604	6174.19653	Yes
39K (KED)	200	10	153774.97585	159356.94326	Yes
44Ca (KED)	200	10	158951.96596	161846.45449	Yes
47Ti (STD)	1	10	79.86481	86.45375	Yes
51V (KED LR)	1	10	18.68685	19.11949	Yes
52Cr (KED)	1	10	130.78229	167.34569	No
55Mn (KED)	3	10	80.79594	83.36175	Yes
56Fe (KED)	19	10	1020.55776	1130.07092	Yes
59Co (KED)	0.5	10	8.00549	8.32734	Yes
60Ni (KED)	0.4	10	48.07315	51.01300	Yes
63Cu (KED)	0.3	10	1.18594	1.76193	Yes
66Zn (KED)	1	10	30.83486	31.08266	Yes
75As (KED)	0.5	10	16.26997	16.42894	Yes
78Se (KED)	1	10	0.66824	0.74870	Yes
88Sr (KED)	1	10	1514.08271	1549.63992	Yes
90Zr (KED)	1	10	23.99564	28.02435	Yes
93Nb (KED)	1	10	0.78032	1.05463	Yes
98Mo (KED)	3	10	4.33851	5.91076	Yes
107Ag (KED)	0.5	10	0.00258	0.00659	Yes
111Cd (STD)	0.07	10	0.06744	0.09002	Yes
111Cd (KED)	0.07	10	0.05158	0.05449	Yes
118Sn (KED)	1	10	19.73747	26.56172	Yes
121Sb (KED)	1	10	6.08505	7.82301	Yes
128Te (KED)	2	10	0.03171	0.03811	Yes
138Ba (KED)	0.2	10	61.19310	63.75662	Yes
182W (KED)	1	10	2.63828	3.12491	Yes
205Tl (KED)	2	10	0.01403	0.00536	Yes
208Pb (KED)	0.2	10	1.88176	1.93370	Yes
209Bi (KED)	0.1	10	0.02384	0.03081	Yes
238U (KED)	0.5	10	0.61558	0.63201	Yes

Table 1: Comparison of hot and cold digests.

From the same sample 4 separate aliquots were taken. These were then filtered and acidified, as above and allowed 48 hours to settle. As above, visible sediment was noticeable after 48 hours of acidification.

Two aliquots were then filtered again to remove the precipitated material producing two pairs of samples each containing one with precipitate and one without. The standard dissolved process was performed on one pair and the total process on the other to identify the impact of including or removing the precipitate in the digest

Results were then compared. Results are as per tables 2 -4 below.

This shows that in all cases where the precipitate is removed a lower Chromium result is achieved indicating that the impact is related only to the Chromium results. This would indicate that either an interference is present on Chromium where the precipitate is not removed, or Chromium is bonded to the coagulant and lost due to the precipitation.

Chromium by ICPMS is analysed at mass 52, as the most commonly abundant isotope. This can be affected by an interference of Ar-C but this should be removed by the Kinetic Energy Discrimination system on the ICP. To ensure this is the case another aliquot was prepared and digested with all the precipitate re-digested. This was then assessed for the major isotope and Cr 53. Consistent results were obtained indicating that a Cr 52 interference is not present in this case. This would indicate that the Cr species in the samples are indeed bonded to the coagulant.



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Element	LOD	Method Precision (%)	Sediment removed Total Digest	Total Digest	Results Consistent
7Li (STD)	3	10	155.38124	152.43921	Yes
9Be (STD)	0.1	10	0.01039	0.00776	Yes
11B (STD)	10	10	1769.33155	1764.38468	Yes
23Na (KED)	76	10	647829.15824	657227.82350	Yes
24Mg (KED)	36	10	38709.29882	39328.02177	Yes
27Al (STD)	10	10	129.99274	132.15062	Yes
31P (KED)	10	10	5887.19189	5946.98386	Yes
39K (KED)	200	10	151982.47647	152080.88306	Yes
44Ca (KED)	200	10	160259.07009	160288.56313	Yes
47Ti (STD)	1	10	83.70167	89.23189	Yes
51V (KED LR)	1	10	18.27975	18.37092	Yes
52Cr (KED)	1	10	129.62554	172.86968	No
55Mn (KED)	3	10	80.12358	81.14502	Yes
56Fe (KED)	19	10	1051.53695	1096.24586	Yes
59Co (KED)	0.5	10	7.66083	8.08906	Yes
60Ni (KED)	0.4	10	49.04410	48.55999	Yes
63Cu (KED)	0.3	10	2.20242	2.39463	Yes
66Zn (KED)	1	10	35.67356	36.90696	Yes
75As (KED)	0.5	10	15.39528	15.71835	Yes
78Se (KED)	1	10	0.34298	0.64644	Yes
88Sr (KED)	1	10	1469.77151	1499.68766	Yes
90Zr (KED)	1	10	25.29081	27.25421	Yes
93Nb (KED)	1	10	2.39556	1.82965	Yes
98Mo (KED)	3	10	4.07203	5.37948	Yes
107Ag (KED)	0.5	10	0.12792	0.04711	Yes
111Cd (STD)	0.07	10	0.06975	0.07618	Yes
111Cd (KED)	0.07	10	0.04811	0.05000	Yes
118Sn (KED)	1	10	18.73087	27.04222	Yes
121Sb (KED)	1	10	5.81180	7.55721	Yes
128Te (KED)	2	10	0.24325	0.14965	Yes
138Ba (KED)	0.2	10	64.33581	64.57747	Yes
182W (KED)	1	10	2.33171	3.15368	Yes
205Tl (KED)	2	10	0.35130	0.03696	Yes
208Pb (KED)	0.2	10	1.96689	1.98247	Yes
209Bi (KED)	0.1	10	0.01841	0.02487	Yes
238U (KED)	0.5	10	0.63841	0.65565	Yes

Table 2: Comparison of Re-Filtered digests of total metals.



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	LOD	Method Precision (%)	Dissolved – sediment removed	Dissolved - not filtered	Dissolved Samples Consistent
7Li (STD)	3	10	150.28576	150.88089	Yes
9Be (STD)	0.1	10	0.00641	0.00977	Yes
11B (STD)	10	10	1719.89326	1726.36723	Yes
23Na (KED)	76	10	636699.50615	637698.59410	Yes
24Mg (KED)	36	10	38181.46866	37919.78202	Yes
27Al (STD)	10	10	123.76775	125.32985	Yes
31P (KED)	10	10	5858.19637	5798.64695	Yes
39K (KED)	200	10	148762.85645	148339.61405	Yes
44Ca (KED)	200	10	157160.61527	155814.53920	Yes
47Ti (STD)	1	10	80.48368	81.89461	Yes
51V (KED LR)	1	10	18.31799	17.61230	Yes
52Cr (KED)	1	10	125.36013	135.85696	Yes
55Mn (KED)	3	10	78.68275	78.88521	Yes
56Fe (KED)	19	10	1013.18929	1039.85796	Yes
59Co (KED)	0.5	10	7.48043	7.75969	Yes
60Ni (KED)	0.4	10	45.60920	46.67866	Yes
63Cu (KED)	0.3	10	1.88807	1.84304	Yes
66Zn (KED)	1	10	32.62512	44.48003	No
75As (KED)	0.5	10	15.17802	15.16306	Yes
78Se (KED)	1	10	0.56713	0.63892	Yes
88Sr (KED)	1	10	1435.32114	1474.33028	Yes
90Zr (KED)	1	10	23.07546	25.04117	Yes
93Nb (KED)	1	10	2.21433	1.43748	Yes
98Mo (KED)	3	10	4.11291	4.06555	Yes
107Ag (KED)	0.5	10	0.12139	0.03724	Yes
111Cd (STD)	0.07	10	0.06237	0.06640	Yes
111Cd (KED)	0.07	10	0.07772	0.04478	Yes
118Sn (KED)	1	10	18.65000	20.63444	Yes
121Sb (KED)	1	10	5.65635	5.98126	Yes
128Te (KED)	2	10	0.23393	0.16300	Yes
138Ba (KED)	0.2	10	62.01579	63.36614	Yes
182W (KED)	1	10	2.49843	2.76002	Yes
205Tl (KED)	2	10	0.55710	0.03360	Yes
208Pb (KED)	0.2	10	1.91560	1.96512	Yes
209Bi (KED)	0.1	10	0.02405	0.02183	Yes
238U (KED)	0.5	10	0.61231	0.60643	Yes

Table 3: Comparison of Re-Filtered digests of dissolved metals.



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	LOD	Method Precision (%)	Dissolved Sediment removed	Sediment removed total	Dissolved Samples Consistent
7Li (STD)	3	10	150.28576	155.38124	Yes
9Be (STD)	0.1	10	0.00641	0.01039	Yes
11B (STD)	10	10	1719.89326	1769.33155	Yes
23Na (KED)	76	10	636699.50615	647829.15824	Yes
24Mg (KED)	36	10	38181.46866	38709.29882	Yes
27Al (STD)	10	10	123.76775	129.99274	Yes
31P (KED)	10	10	5858.19637	5887.19189	Yes
39K (KED)	200	10	148762.85645	151982.47647	Yes
44Ca (KED)	200	10	157160.61527	160259.07009	Yes
47Ti (STD)	1	10	80.48368	83.70167	Yes
51V (KED LR)	1	10	18.31799	18.27975	Yes
52Cr (KED)	1	10	125.36013	129.62554	Yes
55Mn (KED)	3	10	78.68275	80.12358	Yes
56Fe (KED)	19	10	1013.18929	1051.53695	Yes
59Co (KED)	0.5	10	7.48043	7.66083	Yes
60Ni (KED)	0.4	10	45.60920	49.04410	Yes
63Cu (KED)	0.3	10	1.88807	2.20242	Yes
66Zn (KED)	1	10	32.62512	35.67356	Yes
75As (KED)	0.5	10	15.17802	15.39528	Yes
78Se (KED)	1	10	0.56713	0.34298	Yes
88Sr (KED)	1	10	1435.32114	1469.77151	Yes
90Zr (KED)	1	10	23.07546	25.29081	Yes
93Nb (KED)	1	10	2.21433	2.39556	Yes
98Mo (KED)	3	10	4.11291	4.07203	Yes
107Ag (KED)	0.5	10	0.12139	0.12792	Yes
111Cd (STD)	0.07	10	0.06237	0.06975	Yes
111Cd (KED)	0.07	10	0.07772	0.04811	Yes
118Sn (KED)	1	10	18.65000	18.73087	Yes
121Sb (KED)	1	10	5.65635	5.81180	Yes
128Te (KED)	2	10	0.23393	0.24325	Yes
138Ba (KED)	0.2	10	62.01579	64.33581	Yes
182W (KED)	1	10	2.49843	2.33171	Yes
205Tl (KED)	2	10	0.55710	0.35130	Yes
208Pb (KED)	0.2	10	1.91560	1.96689	Yes
209Bi (KED)	0.1	10	0.02405	0.01841	Yes
238U (KED)	0.5	10	0.61231	0.63841	Yes

Table 3: Comparison of Re-Filtered digests of dissolved against total metals.

Conclusion

TM152 has been validated on a variety of matrix and is ran on a variety of samples. This limited situation has not been commonly observed and is not present in the validation set.

For these samples the use of a preservative causes a precipitation that potentially could lower the results for Chromium. Other metals look to be unaffected.

To prevent this issue the samples could be deviated by a filtered preserved sample being analysed for the ALS Total digest method. This would require the clients approval and notification on receipt of samples to enable this non-standard process.