HYDRIDE GENERATION WITH CRYOTRAPPING: DART-MS STUDY OF METHYLATED ARSANES AND ICP-MS ANALYSIS OF TRACE ARSENIC SPECIES IN WATER REFERENCE MATERIALS

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A technique of hydride generation (HG) with subsequent trapping of generated hydrides (cryotrapping, CT) under liquid nitrogen was developed in the early 1970's to improve limits of detection for elements like arsenic and selenium. However, the unique features of this technique make it attractive even for modern analytical chemistry.

DART-MS STUDY OF SELENIUM HYDRIDE AND METHYLATED ARSANES

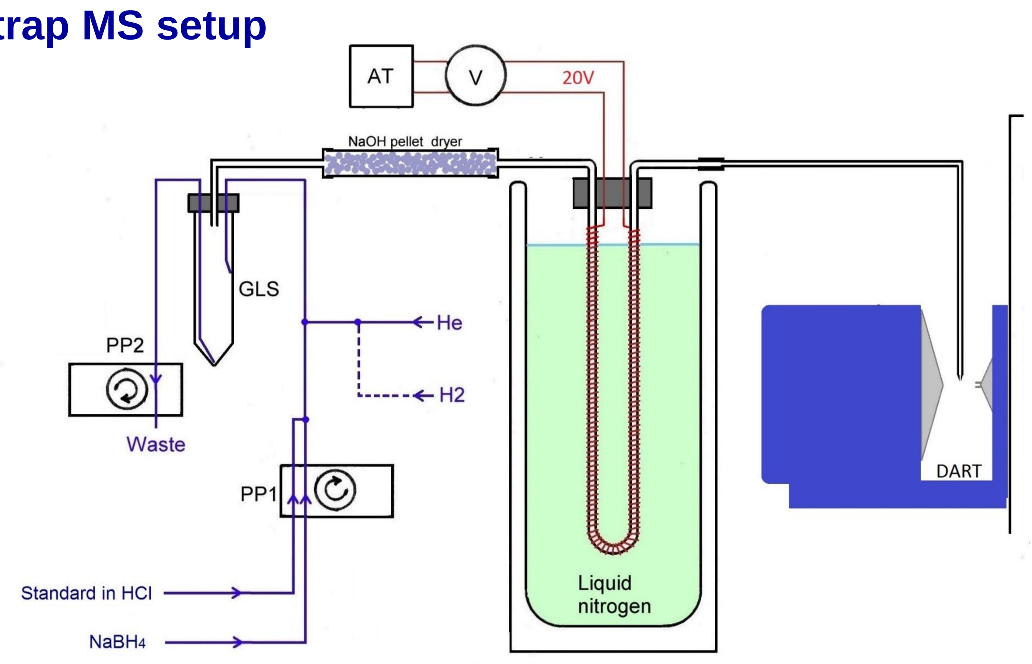
For studies of processes taking place e.g. in hydride generation or atomization, CT can effectively separate the species of interest from other compounds and also from accompanying ballast from HG-spray droplets, vapors and hydrogen. Presented examples are mass spectra of generated selenium hydride, arsane, mono-, di- and trimethylarsane from a DART ionization source coupled with an LTQ-Orbitrap mass spectrometer.

HG-CT- DART- LTQ-Orbitrap MS setup

HG-CT:
Se: 2 ppm in 1 M HCl
0.5% $NaBH_4$ in 0.4% KOH
As species: 1 ppm in 1 M HCl
1% $NaBH_4$ in 0.1% KOH
Flow rates: 1mL/min
Carrier gas He 100 mL/min
Sample volume: 0.5 mL

DART settings:
Needle electrode voltage 3500V
He DART flow rate 3.5 L/min
Discharge & grid electrodes 0V

LTQ-Orbitrap MS settings:
Resolution 15 000
Capillary temperature 100°C
Capillary voltage -35V (negative mode); +65V (positive mode)
Tube lens voltage -45V (negative mode); +100V (positive mode



CONCLUSIONS:

Spectra in both positive and negative ion mode contain mainly the oxidized ions, with the hydride ion not present (As) or present as a minor ion (Se).
Losses of one or more methyl groups are observed for methyl substituted arsanes.
Numerous ions contain multiple As or Se atoms, which do not reflect original species but originate in the ion source. This is more pronounced in HG-CT spectra compared to HG without cryotrap.
Reactions in the ion source must be taken into account in the interpretation of DART spectra for the mechanistic studies of HG.

RESULTS:

SeH_2, negative mode:
Mass spectra taken with a cryotrap, with cryotrap and 15 mL/min H_2 added to simulate H_2 produced from the generator, and directly from hydride generator without a cryotrap.

Mass	Tentative formula	Delta mmu	HG-CT	HG-CT with H2	HG only
80.9263	H Se	2.52	10%	11%	8%
95.9132	O Se	2.57	1%	2%	1%
111.9088	O2 Se	2.66	30%	28%	32%
128.9115	H O3 Se	2.78	67%	41%	44%
144.9061	H O4 Se	2.84	100%	100%	100%
157.9013	O4 N Se	2.79	8%	5%	5%
161.9098	H2 O5 Se	2.89	8%	6%	7%
173.8969	O5 N Se	2.99	12%	7%	4%
192.8340	H O2 Se2	3.25	38%	50%	13%
208.8276	H O3 Se2	3.29	4%	4%	1%
225.8314	H2 O4 Se2	3.36	3%	6%	1%
240.8181	H O5 Se2	3.41	8%	4%	
256.8120	H O6 Se2	3.51	3%	3%	
272.7510	H O2 Se3	3.82	3%	3%	
Most abundant ion count:			5.6E+05	5.8E+05	1.1E+06

Arsines, positive mode:
Mass spectra taken with a cryotrap.

Mass	Tentative Formula	Delta mmu	AsH_3	$MAsH_2$	DMAsH	TMAs
88.9358	C H2 As	-0.71			1%	
90.9153	O As	-0.71		3%		3%
90.9516	C H4 As	-0.72			1%	
100.9361	C2 H2 As	-0.63			1%	4%
102.9518	C2 H4 As	-0.58				8%
104.9675	C2 H6 As	-0.55			11%	10%
105.9627	C H5 N As	-0.58		4%		
106.9468	C H4 O As	-0.44		17%	10%	4%
108.9624	C H6 O As	-0.54		3%		
116.9675	C3 H6 As	-0.49				2%
118.9832	C3 H8 As	-0.44				4%
120.9989	C3 H10 As	-0.41			2%	7%
136.9943	C3 H10 O As	-0.28				79%
137.9653	C2 H7 O2 As	-0.32				2%
138.9728	C2 H8 O2 As	-0.15			100%	100%
140.9526	C H6 O3 As	-0.15		100%		4%
142.9317	H4 O4 As	-0.28	100%	9%		
154.9683	C2 H8 O3 As	-0.07		3%	3%	
164.8660	C H3 As2	-0.11		13%		
168.9842	C3 H10 O3 As	0.17		12%	1%	
178.8820	C2 H5 As2	0.19			1%	
194.9130	C3 H9 As2	-0.03		4%	6%	
196.8560	C H3 O2 As2	0.02		6%		
198.8352	H O3 As2	0.03	7%	2%		
210.9082	C3 H9 O As2	0.21			4%	4%
212.8874	C2 H7 O2 As2	0.12		3%		
214.8666	C H5 O3 As2	0.11		2%		
216.8457	H3 O4 As2	-0.05	6%			
224.9603	C5 H15 As2	0.26				4%
226.9396	C4 H13 O As2	0.33			8%	6%
228.8822	C2 H7 O3 As2	0.01		6%		
230.8615	C H5 O4 As2	0.08		11%		
232.8406	H3 O5 As2	-0.11	11%			
232.8772	C H7 O4 As2	0.15		2%		
234.8549	H5 O5 As2	-0.05	2%			
242.9345	C4 H13 O2 As2	0.34				2%
244.9140	C3 H11 O3 As2	0.50			12%	
246.8929	C2 H9 O4 As2	0.21		5%		
248.8722	C H7 O5 As2	0.25		6%		
250.8512	H5 O6 As2	-0.02	8%			
254.8114	C2 H6 As3	0.23		6%		
256.9503	C5 H15 O2 As2	0.41				20%
258.9297	C4 H13 O3 As2	0.61			12%	48%
260.9091	C3 H11 O4 As2	0.68				5%
262.8879	C2 H9 O5 As2	0.27		4%		
264.8672	C H7 O6 As2	0.31		2%		
266.8464	H5 O7 As2	0.24	3%			
270.8428	C3 H10 As3	0.28		5%		
286.8378	C3 H10 O As3	0.42		2%		
332.8440	C4 H12 O3 As3	1.08			1%	
336.8019	C2 H8 O5 As3	0.47		3%		
338.7812	C H6 O6 As3	0.54		2%		
344.7567	C3 H9 As4	0.39		3%		
348.8388	C4 H12 O4 As3	0.98			2%	
364.8701	C5 H16 O4 As3	1.02			2%	
Most abundant ion count:			1.5E+06	7.0E+06	1.7E+07	1.5E+07

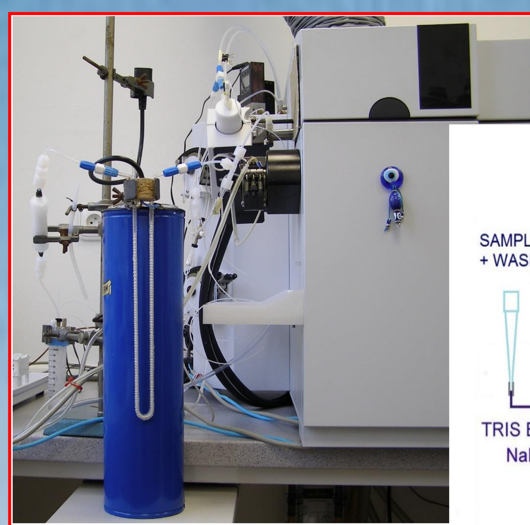
Arsines, negative mode:
Mass spectra taken with a cryotrap.

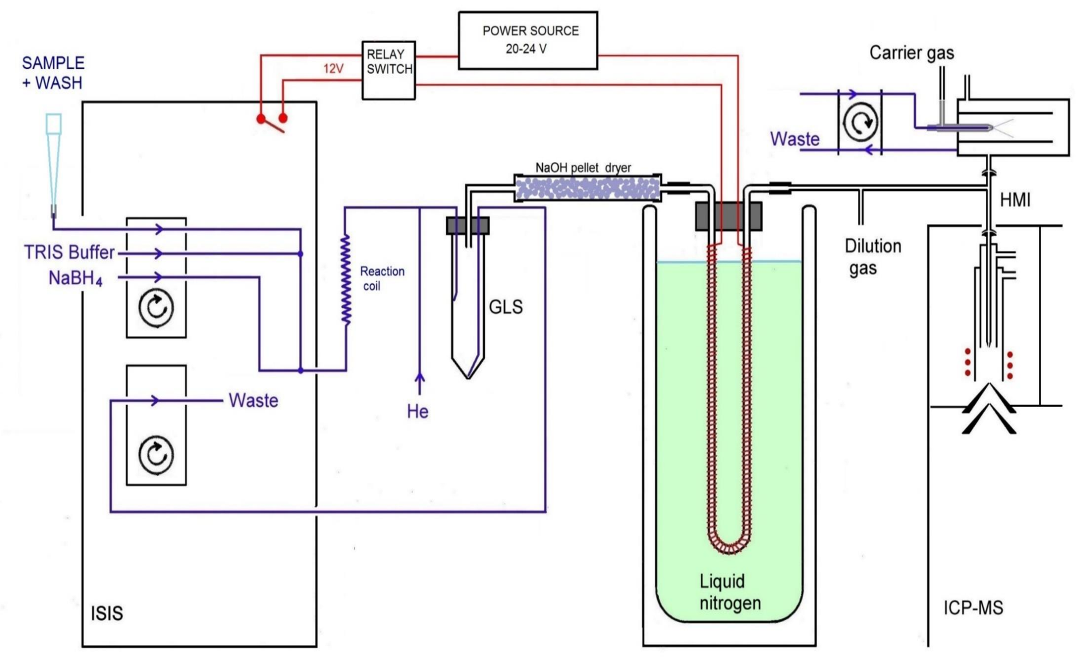
Mass	Tentative Formula	Delta mmu	AsH_3	$MAsH_2$	DMAsH	TMAs
106.9133	O2 As	2.64	10%	6%	5%	3%
122.9080	O3 As	2.82	9%	13%	13%	8%
123.9159	H O3 As	2.79	3%	5%	4%	
124.9247	H2 O3 As	2.72	19%	14%	7%	4%
136.9612	C2 H6 O2 As	2.88			65%	100%
137.9634	C H3 O3 As	2.90			4%	
138.9395	C H4 O3 As	2.87		31%	100%	61%
139.9109	C H4 O3 As	2.84	11%	9%	6%	
140.9191	H2 O4 As	2.86	100%	100%	73%	32%
153.9142	H O4 N As	2.81	14%	13%	8%	
154.9350	C H4 O4 As	2.87		4%	8%	5%
155.9056	H O5 As	2.83	7%	6%	4%	
156.9135	H2 O5 As	2.99	5%	7%	4%	
157.9223	H3 O5 As	2.87	4%	3%		
158.9302	H4 O5 As	2.86	7%	6%	4%	
160.9013	H3 O3 As Cl	2.90	4%		3%	
167.9433	C2 H5 O4 As	3.03			7%	15%
168.9509	C2 H6 O4 As	3.02			5%	14%
169.9584	C2 H7 O4 As	3.02			28%	46%
171.9384	C H5 O5 As,H3 O5	3.02	12%	12%	33%	18%
172.9376	C2 H7 O2 As Cl	3.05			9%	11%
173.9177	H3 O6 As	2.94	23%	23%	14%	6%
174.9167	C H5 O3 As Cl	2.90			22%	11%
176.8962	H3 O4 As Cl	2.94	11%	4%	13%	8%
182.9658	C3 H8 O4 As	2.95				4%
183.9609	C2 H7 O4 N As	3.05			22%	33%
184.9452	C2 H6 O5 As	3.17				4%
185.9412	C H5 O5 N As	3.05		9%	29%	13%
186.9607	C2 H8 O5 As	2.99	4%		3%	
187.9204	H3 O6 N As	3.01	13%	14%	10%	4%
196.9826	C4 H10 O4 As	3.05				7%
198.9609	C3 H8 O5 As	3.02			3%	
199.9570	C2 H7 O5 N As	3.10			7%	12%
201.9348	C2 H7 O6 As	3.07		8%	29%	12%
202.9206	C H4 O7 As	3.14	4%	4%		
203.9157	H3 O7 N As	3.10	18%	16%	21%	12%
214.8321	H O4 As2	3.00	4%	6%		
228.8485	C H3 O4 As2	3.11		13%	15%	
229.8194	O5 As2	3.18		3%		
230.8283	H O5 As2	3.21	15%	24%	8%	
232.8446	H3 O5 As2	3.27	9%	11%		
242.9012	C3 H9 O3 As2	3.30			9%	
244.8811	C2 H7 O4 As2	3.43		15%	51%	9%
246.8589	C H5 O5 As2	3.34		48%	43%	4%
247.8318	H2 O6 As2	3.35		4%		
248.8401	H3 O6 As2	3.39	32%	40%	15%	
258.8955	C3 H9 O4 As2	3.45			48%	32%
259.8676	C2 H6 O5 As2	2.99		7%	16%	
260.8739	C2 H7 O5 As2	3.53		11%	72%	23%
261.8476	C H4 O6 As2	3.37		19%	14%	
262.8557	C H5 O6 As2	3.45		26%	47%	9%
263.8276	H2 O7 As2	3.41	7%	9%		
264.8342	H3 O7 As2	3.43	24%	30%	22%	4%
273.8707	C2 H6 O5 N As2	3.49			5%	
274.9285	C4 H13 O4 As2	3.49			10%	29%
275.8989	C3 H10 O5 As2	3.39			3%	
276.9057	C3 H11 O5 As2	3.63			15%	13%
278.8868	C2 H9 O6 As2	3.43			8%	7%
279.8570	H4 O8 As2	3.47		3%	22%	
280.8644	C H7 O7 As2	3.41		4%	5%	
281.8378	H4 O8 As2	3.47	5%	7%		
289.9151	C2 H6 O6 N As2	3.53			3%	4%
291.8454	C H4 O7 N As2	3.55		4%	6%	
309.8576	C H6 O8 N As2	3.64			3%	
311.8327	H4 O9 N As2	3.41	3%	3%		
320.7743	C H4 O5 As3	3.69		8%		
322.7541	H2 O6 As3	3.76	5%	9%		
325.8517	C H6 O9 N As2	3.69			4%	
334.7911	C2 H6 O5 As3	4.03		9%	6%	
336.7669	C H4 O6 As3	3.77		29%	9%	
338.7460	H2 O7 As3	3.88	10%	19%	4%	
350.7823	C2 H6 O6 As3	3.90		8%	12%	
352.7614	C H4 O7 As3	3.91		19%	16%	
354.7420	H2 O8 As3	4.17	9%	13%	5%	
356.7598	H4 O8 As3	4.20		5%		
366.8141	C3 H10 O6 As3	3.79			16%	
368.7967	C2 H8 O7 As3	4.08		10%	19%	
370.7738	C H6 O8 As3	4.00		9%	7%	
372.7560	H4 O9 As3	4.32	3%	4%		
382.8134	C3 H10 O7 As3	4.18			6%	
384.7904	C2 H8 O8 As3	4.03		5%	12%	
386.7712	C H6 O9 As3	4.39		4%	7%	
400.8209	C3 H12 O8 As3	4.26			5%	
402.7987	C2 H10 O9 As3	4.12			7%	
404.7789	C H8 O10 As3	4.13			3%	
444.6902	C H5 O8 As4	4.78		4%		
458.7016	C2 H7 O8 As4	3.45		3%		
Most abundant ion count:			9.9E+05	9.6E+05	3.8E+05	5.6E+05

ICP-MS ANALYSIS OF TRACE ARSENIC SPECIES IN WATER REFERENCE MATERIALS

HG-CT offers the possibility of preconcentration of analyte from large sample volumes, as well as the ability to separate individual species. This is ideal for speciation analysis at ultratrace levels, which is one of the current challenges of elemental analytical chemistry. For many matrices, minimal sample pretreatment is required, which reduces sample dilution and risk of contamination.
The analysis of inorganic and methylated arsenic species is shown as an example of the sensitive detection achieved with HG-CT coupled to quadrupole ICP-MS.

HG-CT-ICP-MS setup





HG-CT
0.75M Tris.HCl buffer, pH 6
1% $NaBH_4$ in 0.1% KOH
Flow rate: 1mL/min
Carrier gas He 75 mL/min
Sample volume: 0.5 ml

ICP-MS
Agilent 7700x with ISIS unit
Power: 1600 W
Carrier gas: Ar 0.6 L/min
Dilution gas: 0.55 L/min
Collision cell: He 3.5 ml/min
75As
IS 125Te 100 ng/mL, nebulized

Step		Time s	Pumps 1	Pumps 2	U-tube Cooled	U-tube Heating
1	U-tube precool & sample inject	30	-	ON	ON	-
2	Hydride generation	75	ON	-	ON	-
3	HG system gas flush	85	-	-	ON	-
4	U-tube heat & data acquisition	80	-	-	-	ON
5	U-tube drying & waste liquid removal	85	-	ON	-	ON

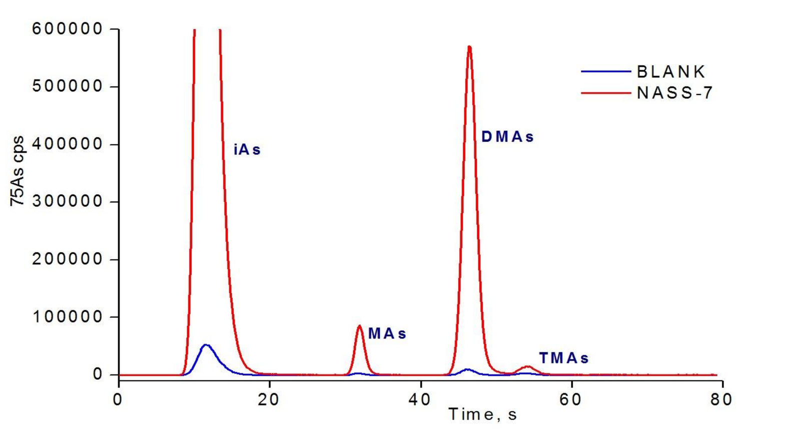
For complete method description see: Matoušek *et al*, JAAS., **28** (2013), 1456 – 1465.

RESULTS:

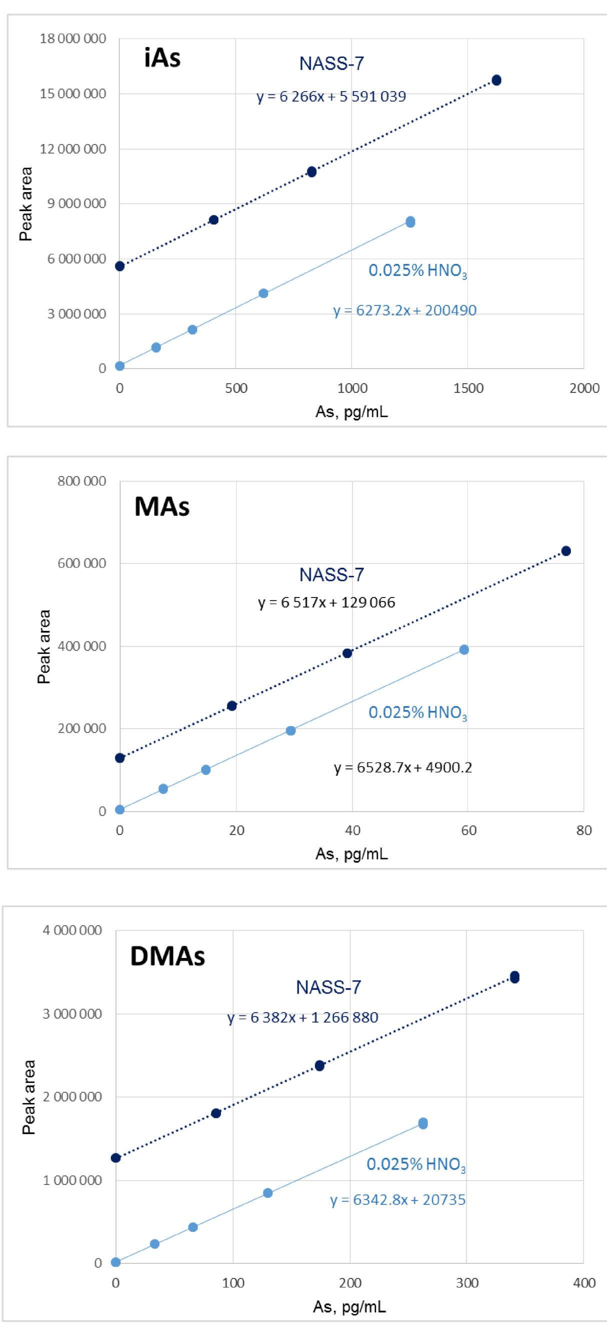
Arsenic speciation in the new certified reference materials of river, sea and drinking water

		iAs ng/L	(sd)	MAs ng/L	(sd)	DMAs ng/L	(sd)	TMAsO ng/L	(sd)	Sum of species ng/L	Certified As ng/L
SLRS-6	Riverine water	**362**	(4.1)	**75**	(2.3)	**73**	(2.8)	**21**	(1.1)	**531**	**570 ± 80**
NASS-7	Seawater	**846**	(4.6)	**19**	(0.4)	**193**	(1.9)	**13**	(0.3)	**1 071**	**1230 ± 60**
CASS-6	Seawater	**499**	(7.2)	**20**	(0.8)	**199**	(2.6)	**24**	(0.3)	**741**	**1040 ± 100**
AQUA-1	Drinking water	**124**	(2.0)	**36**	(0.9)	**28**	(1.9)	**13**	(0.3)	**201**	**not available yet**

The reference materials were analyzed after prereduction with 0.1g solid L-cysteine hydrochloride per 5 ml (iAs, MAs, DMAs) or without prereduction (TMAsO). Triplicate analyses of 3 subsamples of 3 bottles were analyzed against 5 point calibration for all species prepared in 0.025% HNO_3.



Matrix influence was checked by matching slopes of standard addition for all species in all materials.



NASS-7		L-cysteine prereduced iAs pg/ml	MAs pg/ml	DMAs pg/ml	Not prereduced TMAsO pg/ml
Bottle 1	Subsample 1	852	18.9	196	12.1
		851	18.7	197	12.4
		852	18.6	196	12.7
	Subsample 2	847	18.7	194	13.1
		847	18.6	194	13.3
		852	18.7	195	13.1
	Subsample 3	848	18.7	194	13.2
		852	18.9	195	13.1
		845	18.8	195	13.3
Bottle 2	Subsample 1	849	18.1	195	12.9
		852	18.1	194	12.9
		851	18.1	194	13.0
	Subsample 2	844	19.5	193	13.4
		839	19.5	193	13.3
		839	19.5	192	13.2
	Subsample 3	842	19.0	191	13.0
		849	19.0	193	13.2
		848	18.9	195	13.1
Bottle 3	Subsample 1	848	18.3	188	12.9
		845	18.8	193	12.8
		842	18.7	192	13.1
	Subsample 2	847	18.4	192	13.4
		838	18.2	192	13.4
		838	18.1	192	13.3
	Subsample 3	843	18.9	192	13.1
		842	19.1	192	13.1
		846	19.1	193	13.2
	Average	846	18.7	193	13.1
	RSD	0.5%	2.2%	1.0%	2.2%

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