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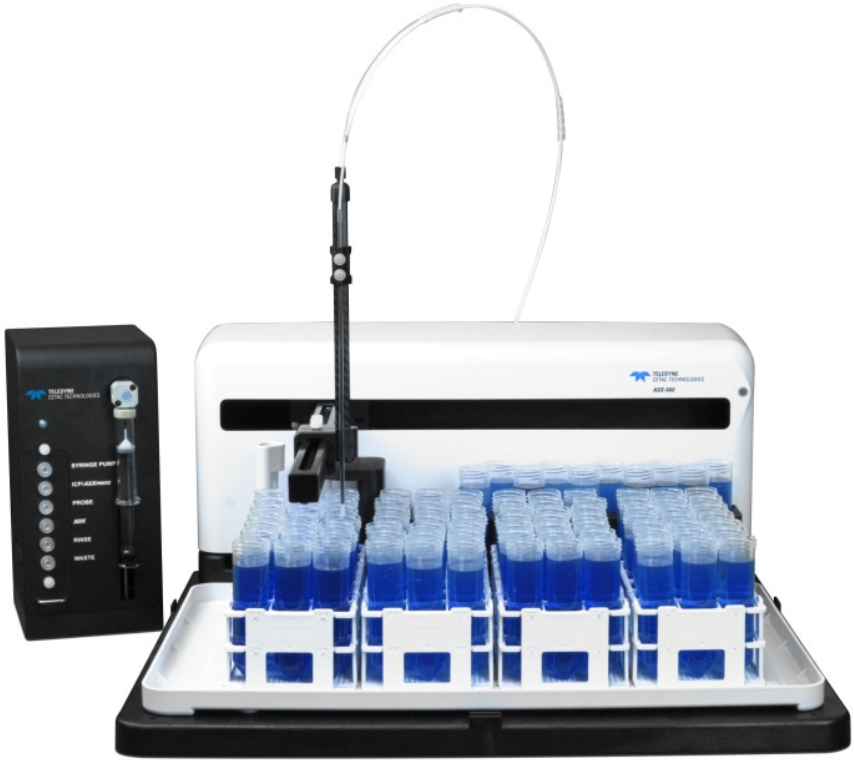
Application Note

Automating EPA Method 200.8 using the SDXHPLD High Performance Liquid Dilution System

Jim Maximovich, Teledyne CETAC Technologies, Omaha, NE, USA, Jim.Maximovich@Teledyne.com



The SDX HPLD system combines the proven ASX-560 autosampler with a novel vortex mixing dilution accessory, enabling prescriptive and intelligent dilution of samples up to a factor of 5000X.

The SDX employs vortex mixing to promote homogenization of a sample to ensure accurate and precise analysis following dilution. The variety of sample matrices and concentrations submitted for trace elemental analysis by EPA Method 200.8 necessitates the need for large dilution factors.

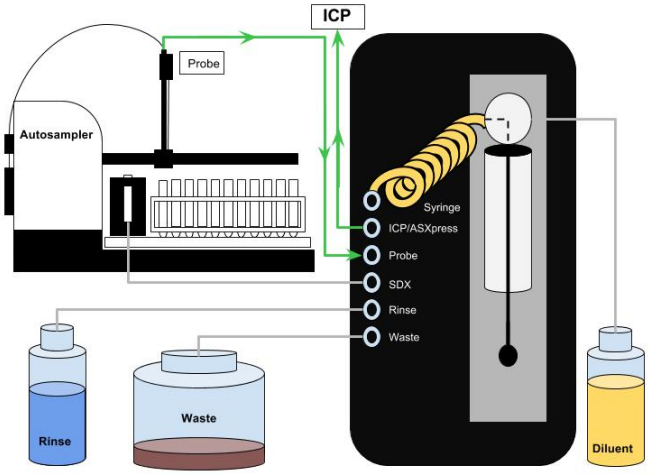
Functionality

The SDX HPLD system when combined with Thermo Scientific™ Qtegra™ ISDS Software is capable of prescriptive and intelligent dilution up to a factor of 5000X.

The prescriptive dilution function is capable of creating calibration lines from one stock standard as well as prescriptively diluting samples. The intelligent dilution function allows the user to correct QC failures within the method by auto diluting samples with internal standard values beyond the user defined range as well as auto diluting samples that give intensities beyond the linear dynamic range.

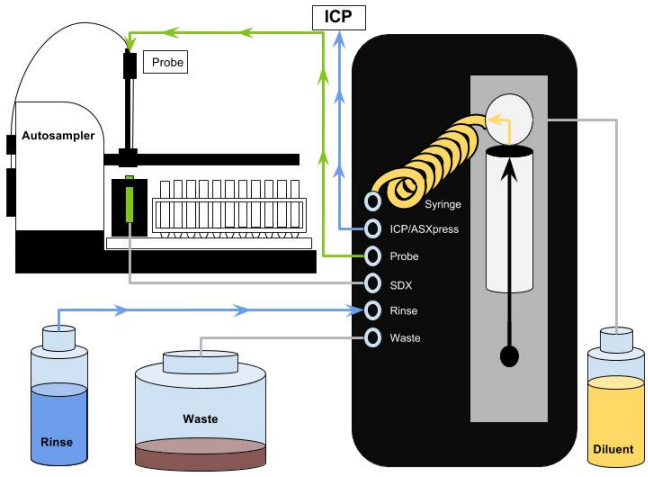
Normal Operation

During normal operation the autosampler probe draws a sample through the SDX module and directs it to the ICP.

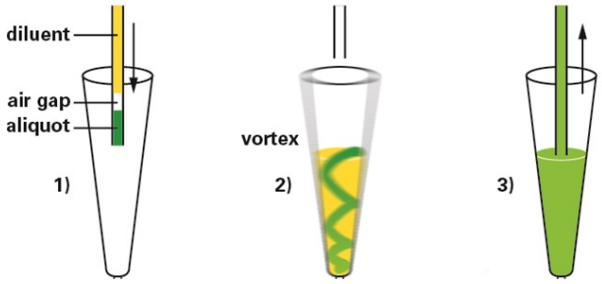


Dilution and Mixing

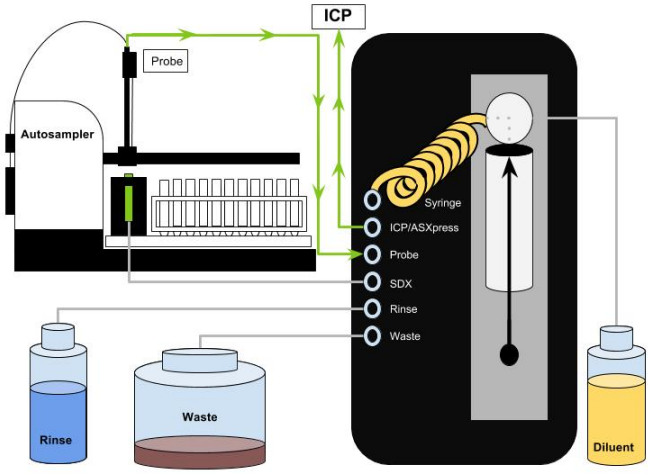
1. For a dilution, the sample probe is connected to a high resolution syringe pump for aliquot, air gap and diluent addition to the vortex mixing vessel.



2. The vortex mixing vessel then performs multiple pulsed vortex cycles to create a thoroughly homogenized sample.

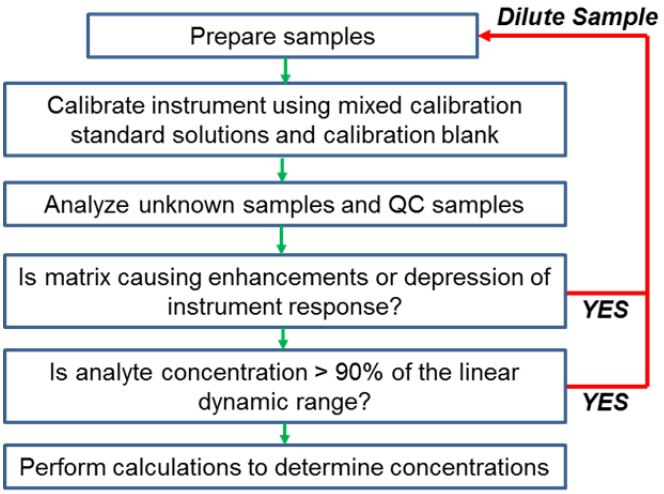


3. Sample uptake into the ICP-MS/ICP-OES can be either via loop loading with Sprint valve/*ASXPRESS PLUS* systems or via peristaltic pump.



EPA Method 200.8 Laboratory Workflow

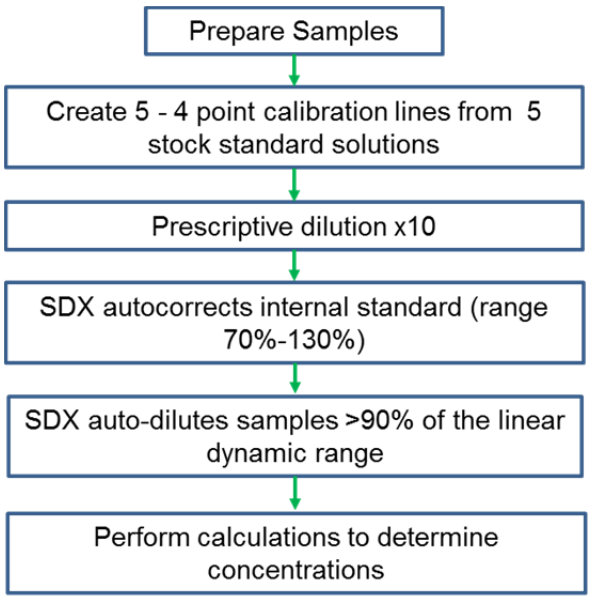
High throughput laboratories report up to 25% of samples per run requiring re-analysis due to samples being above the linear dynamic range or matrix effects causing suppression or enhancement to the internal standard response. This is a major cause of loss of lab productivity.



EPA Method 200.8 requires all analyzed samples to have concentrations less than 90% of the linear dynamic range as well as matrices that do not cause suppression or enhancements effects to the internal standard. With the wide range of sample types that high throughput laboratories encounter, re-analysis of samples is difficult to avoid.

Automating EPA Method 200.8

By utilizing the SDX HPLD to carry out EPA Method 200.8 you combine sample dilution and sample introduction to remove all re analysis of samples due to QC failures. This increases the efficiency and profitability of the laboratory.



Productivity

The addition of the SDX high performance dilution system to the sample preparation and sample introduction gives significant productivity benefits. The addition of the SDX decreases human errors associated with sample handling. It decreases the time and solutions used to create calibration lines. Contamination sources from collection to detection. The SDX removes sample re-runs due to samples having concentrations above the defined linear dynamic range or if samples have matrices that suppress or enhance internal standard intensity. The SDX system increases precision, accuracy and throughput by the increase in capability. The online dilution capability enables samples to be loaded and for the operator to walk away and carry out other duties. The increase in traceability of the prescriptive and intelligent dilutions enables laboratory to automate the traceability of the system. By removing re-runs and making the laboratory workflow more efficient results are able to be reported quicker to your customers. This enhances throughput and therefore making the laboratory more profitable.

Method Detection Limits

The limit of detection (LOD) and limit of quantifications (LOQ) were calculated by performing an analysis of a blank sample with 10 replicates

- The LOD was calculated as 3 x the standard deviation of the repeats
- The LOQ was calculated as 10 x the standard deviation of the repeats
- This analysis was performed 3 times and an average taken

Table 1. Method Detection Limits (µg/L)

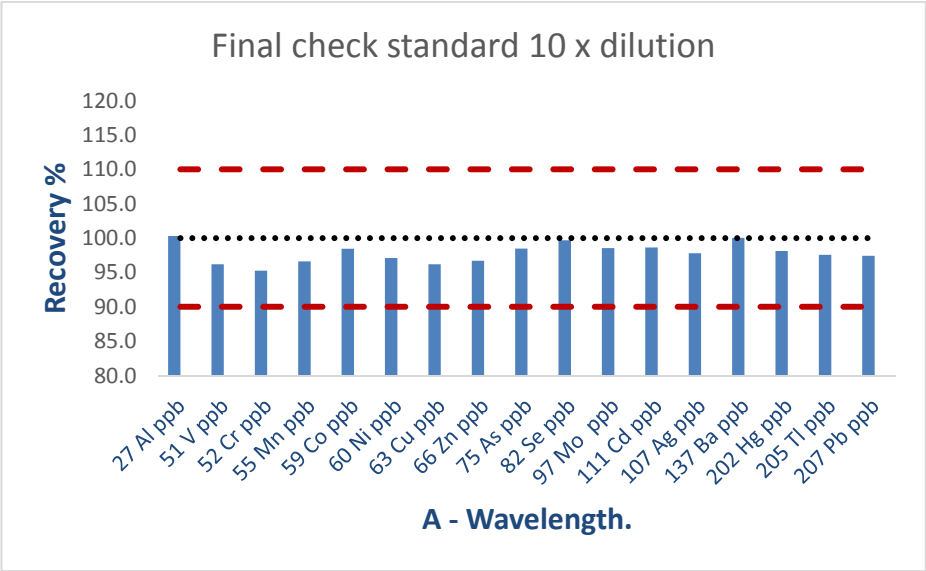
Element	Al	As	Ba	Cr	Co	Cu
LOD	0.06	0.29	0.29	0.044	0.007	0.014
LOQ	0.20	0.96	0.95	0.14	0.024	0.047

Element	Cd	Ni	Mo	Pb	Se	Hg
LOD	0.004	0.067	0.025	0.009	0.019	0.085
LOQ	0.013	0.22	0.08	0.03	0.064	0.28

Element	Tl	V	Zn
LOD	0.016	0.018	0.033
LOQ	0.053	0.059	0.11

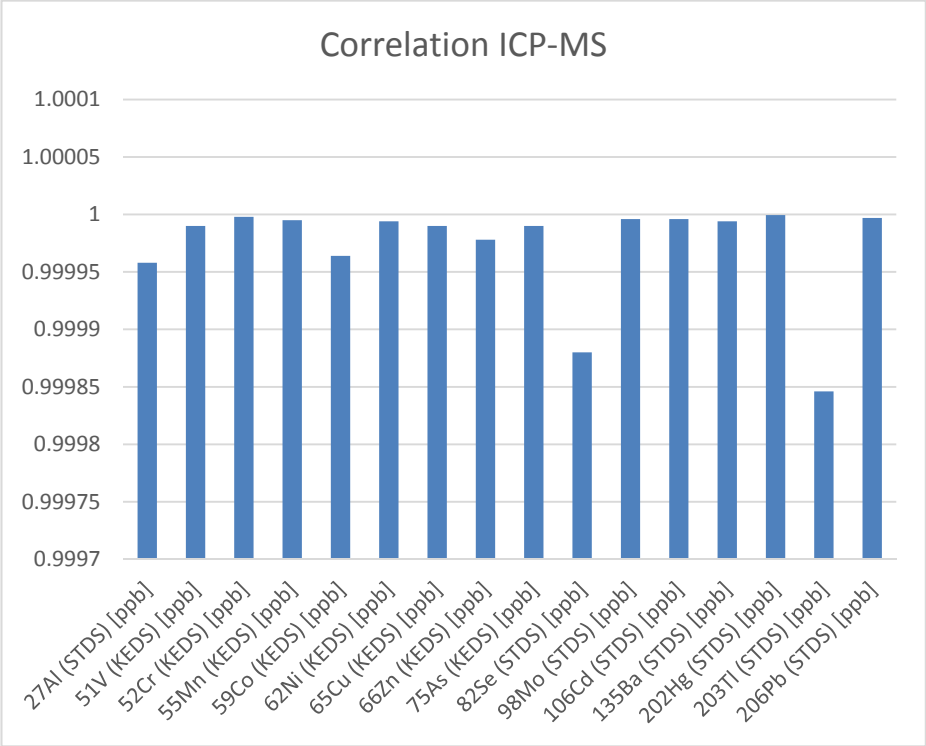
Accuracy and Precision

A 100 ppb standard was diluted 10 x and was analyzed 3 times. The average was taken to demonstrate the precision and accuracy of the system. The plot demonstrates that the recovery is within 3% for all elements. RSD % values for the results were also less 10%



Correlation

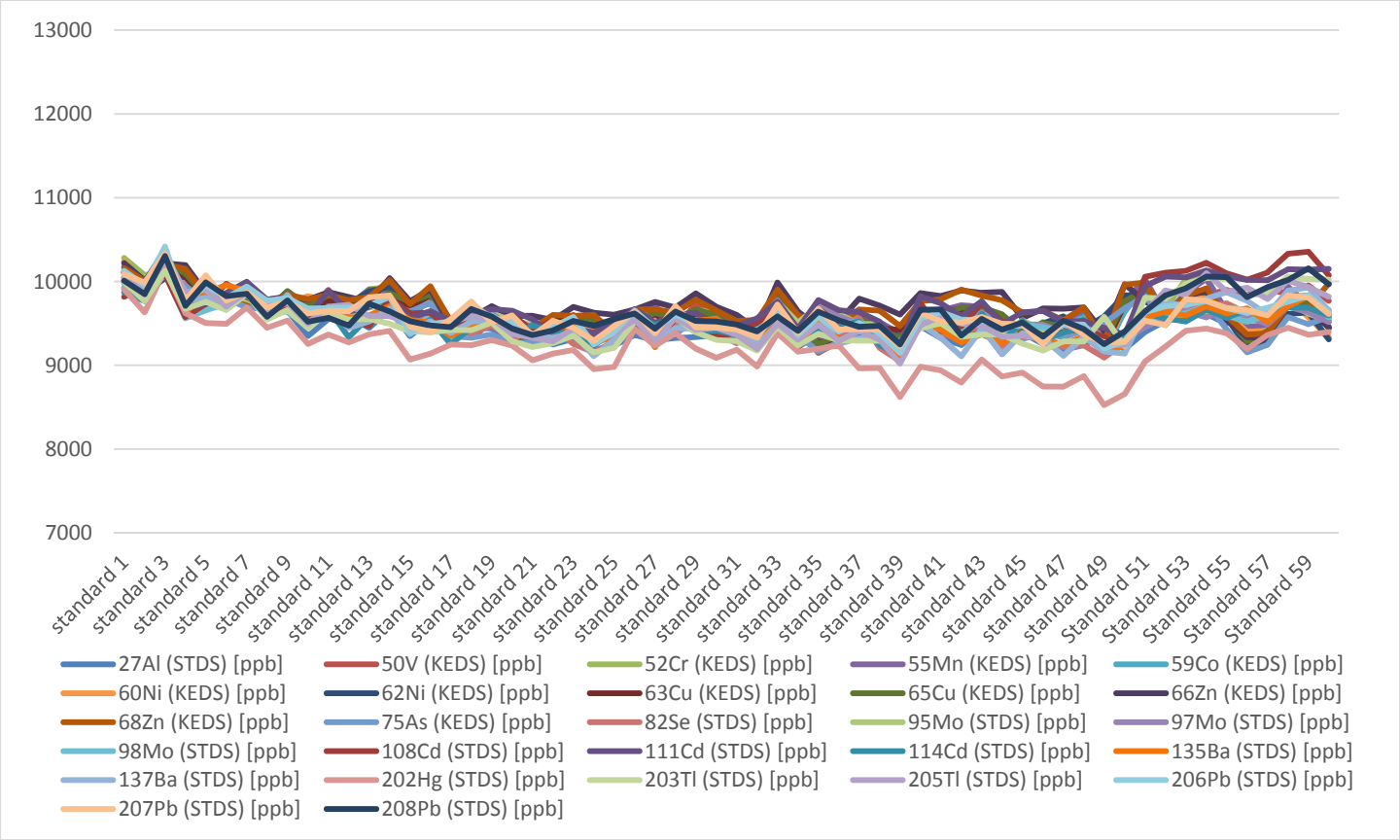
The automatic creation of a calibration line displays excellent correlation for a wide range of elements. Displayed here we have the correlation of a 5 point calibration line created using the SDX on the iCAP RQ ICP-MS system from a 1 ppm multi element standard solution. The majority of elements display a 0.9999 correlation line while Thallium and Selenium are just below this value.



SDXHPLD Robustness, Ruggedness and Intermediate Precision

Robustness is an assay measurement that remains unaffected by deliberate changes to the method. Ruggedness is the reproducibility of the data under normal but variable conditions (such as different operators or instruments used). Intermediate Precision is to cover the various influences within a laboratory, i.e. conducting analyses on two different days. This is to examine the effects of random events on the precision of an analytical method. Intermediate Precision therefore gives a first indication already of the future transferability of an analytical method. Not a lot of change when run on different days and with a deliberate change in the RF watts on day two. This shows that data is unaffected by the SDX. Intermediate precision is also satisfied here because the data differs by less than 10 % (except Hg) there is some observed instrument drift.

A 200 x dilution was performed on a 10,000 ppb standard. Run with 30 replicates on two different days with identical SDXHPLD prepared curves. The intelligent dilution performed was a 10 x followed by a 20 x for a total 200 x dilution.



Robust-Watts changed | Ruggedness-data run on day 2 with different (new peristaltic pump) tubing | Intermediate Precision- Data run on 2 different days

Analysis: EPA 200.8

Here we display the concentration values of elements that were diluted by the SDX to bring them back into the calibration range. Zn and As were not diluted because they are within the calibration range. The LCS, MS and MSD are samples we obtained from a certified 200.8 EPA laboratory. The samples were prepped according to SW-846 6020 EPA methodologies.

Label	59Co KEDS ppb	60Ni KEDS ppb	63Cu KEDS ppb	109Ag STDS ppb	111Cd STDS ppb	67Zn KEDS ppb	55Mn KEDS ppb	27Al STDS ppb
Blank	-0.213	-0.359	-0.397	-0.022	-0.424	0.599	-0.331	-0.72
STD 1	4.992 (5.000)	4.976 (5.000)	4.924 (5.000)	1.226 (1.250)	4.704 (5.000)	12.579 (12.500)	4.951 (5.000)	25.023 (25.000)
STD 2	10.011 (10.000)	10.036 (10.000)	10.114 (10.000)	2.537 (2.500)	10.444 (10.000)	24.881 (25.000)	10.073 (10.000)	49.966 (50.000)
STD 3	19.996 (20.000)	19.988 (20.000)	19.962 (20.000)	4.988 (5.000)	19.852 (20.000)	50.040 (50.000)	19.976 (20.000)	100.011 (100.000)
LCS @ 40 ppb	43.958	43.656	44.292	45.182	42.939	42.569	45.001	37.934
LCS by intelligent dilution	38.824	38.402	39.612	43.371	40.223	N/A	38.311	N/A
% Recovery pre dilution	109.9	109.1	110.7	113.0	107.3	106.4	112.5	94.8
% Recovery post dilution	97.1	96.0	99.0	108.4	100.6	N/A	95.8	N/A

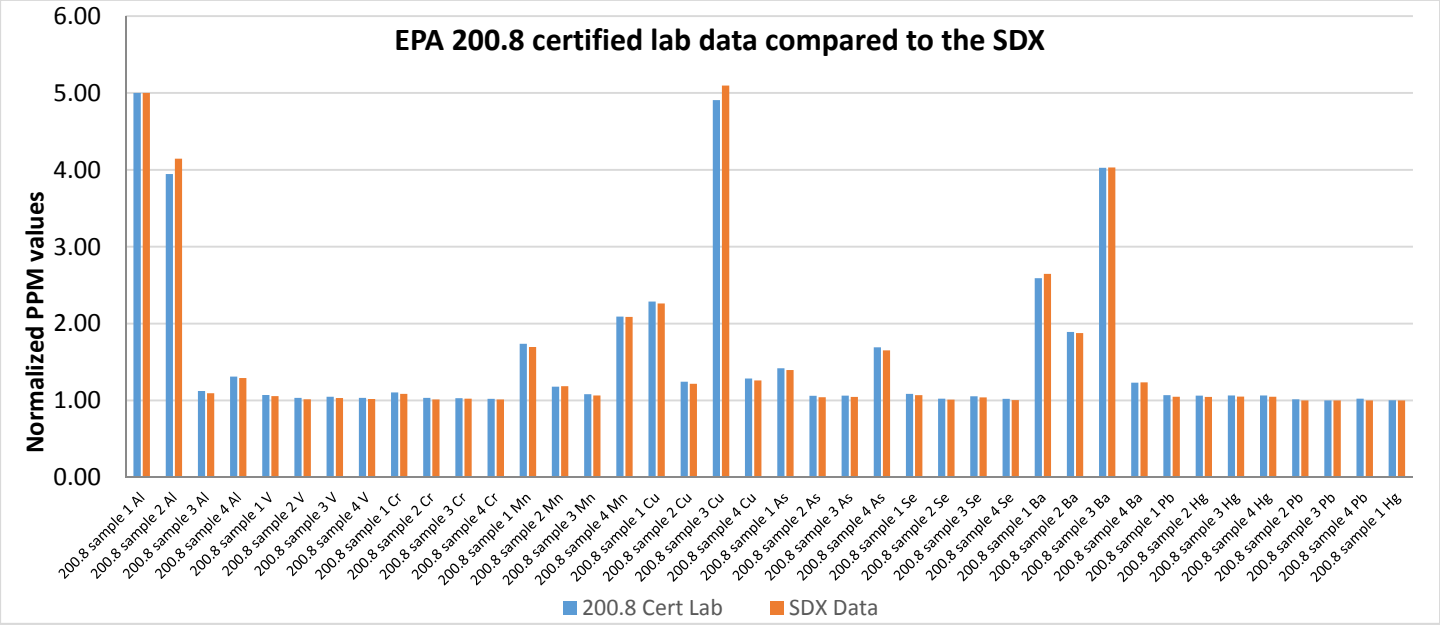
Label	59Co KEDS ppb	60Ni KEDS ppb	63Cu KEDS ppb	109Ag STDS ppb	111Cd STDS ppb	67Zn KEDS ppb	55Mn KEDS ppb	27Al STDS ppb
200.8 sample	0.716	7.521	42.709	0.01	-0.168	45.853	24.462	104.378
200.8 sample Intelligent Dilution	N/A	N/A	45.744	N/A	N/A	N/A	24.715	106.224
200.8 sample Matrix spike @40 ppb	39.74	45.041	77.751	34.393	33.757	84.691	67.442	156.811
200.8 sample Intelligent Dilution MS	39.88	45.907	87.506	40.932	38.966	83.779	67.745	146.666
200.8 sample Matrix Spike Dup @ 40 ppb	37.771	42.887	74.182	33.82	32.798	81.743	64.241	153.196
200.8 sample Intelligent Dilution MSD	41.355	47.354	90.599	42.096	40.168	85.565	70.563	151.864
% Recovery pre dilution MS	97.6	93.8	87.6	86.0	84.8	97.1	107.5	131.1
% Recovery post dilution MS	97.9	96.0	104.4	102.3	97.8	94.8	107.6	101.1
% Recovery pre dilution MSD	92.6	88.4	78.7	84.5	82.4	89.7	99.4	122.0
% Recovery post dilution MSD	101.6	99.6	112.1	105.2	100.8	99.3	114.6	114.1

* 95% of all the data derived from intelligent dilutions produced better results.

Figure: SDX intelligent dilutions on 200.8 LCS, MS & MSD. Dilutions provide a 10% improvement in recovery. Elements within the calibration curve are not diluted.

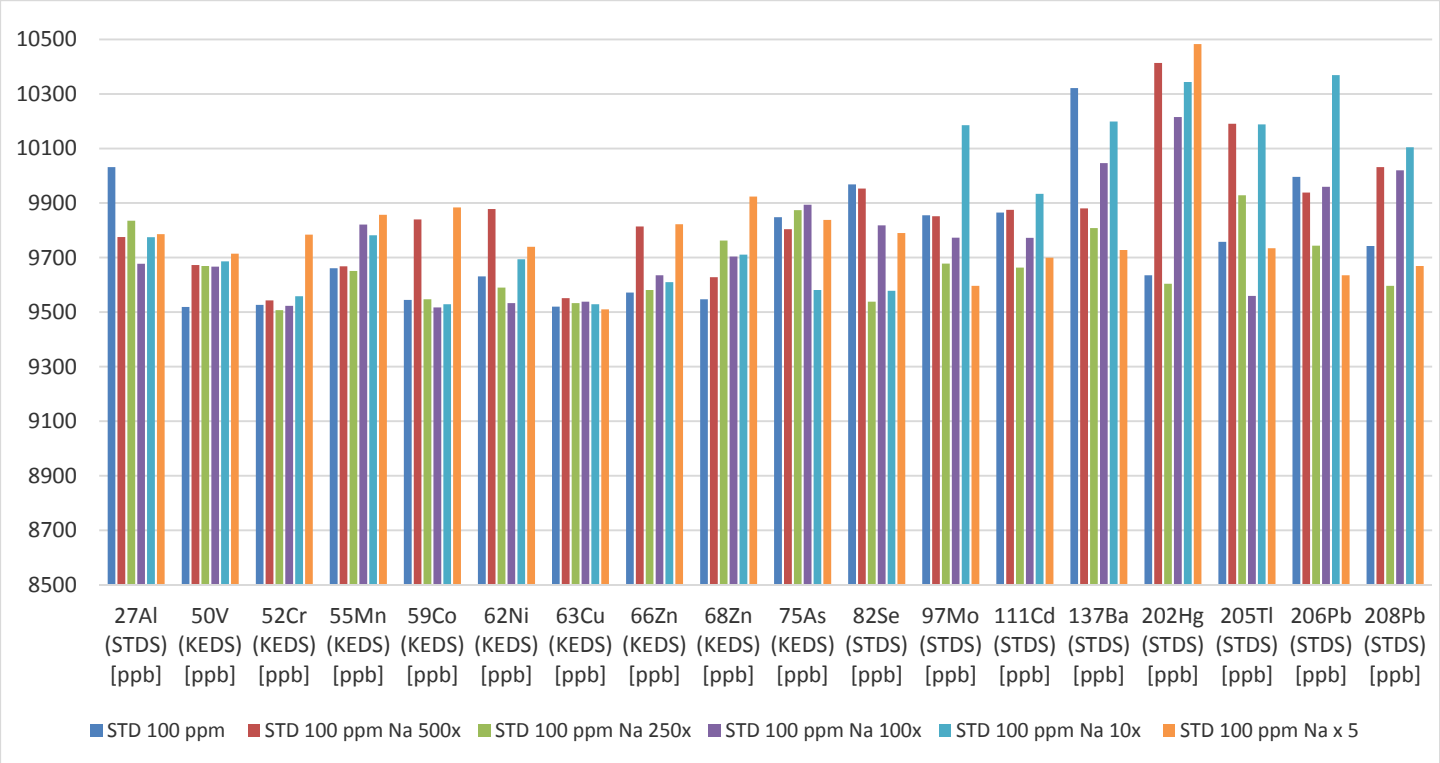
System suitability with SDX dilution

System suitability confirms method validation and proper instrument performance by checking a known value at the start of a run or during the run. In this case we show that we can obtain the same known values from some samples obtained by an EPA certified 200.8 lab. The samples in red were reported by SDX intelligent dilution.



SDX$_{HPLD}$ Specificity

Specificity is the ability to quantify and identify target analytes in the presence of components which could or are expected to be present. Here we demonstrate that the SDX is able to do serial dilutions on a sample containing 100 ppm Na and successfully quantifying the target analytes within 5% of the original 10,000 ppb standard. Target analytes quantitatively obtained in the presence of high Sodium at serial dilutions.



Target analyte qualitative obtained in the presence of high sodium in serial dilutions. All analytes except Hg with 2% RSD.

Prescriptive Dilution

The creation of a calibration line from one stock standard solution within QTEGRA is very easy to carry out. First the concentrations for the analytes within the stock standard solution must be defined before proceeding to the sample list part of the software, as is displayed here. First, a calibration blank is defined which is labelled Blank 1 in this case and is situated in standard position 3. The sample Type must be defined as a blank for the software to recognize it as the first point within the calibration. Next we create the standards, in this case we have standards 1 -7 all defined as being in standard position 1. In sample type we define these as standards for the software to know that these values will form the calibration line. You must also define the particular stock standard which the standard is being made from which was defined within the standards tab. You can also define multiple standards if you wish to separate different analytes due to chemical incompatibility. In order to complete the calibration line it is necessary to choose decreasing autodilution factors ending with the top standard. The concentrations of the analytes defined in the standard tab are divided by the autodilution factor to give the expected concentration response within the software.

The prescriptive dilution capability can also be applied to samples. In the example displayed above the USGS Geo-standard AGV-2 has been manually diluted by 1000 prior to analysis and we have told the system to carry out a 10 x dilution on this sample giving a total dilution factor of 10000.

	Label	Status	Rack	Vial	Sample Type	Standard	Autodilution Factor
1	blank		Standard	1	BLK		1
2	2ppm		Standard	3	STD	Na	5000
3	2.5ppm		Standard	3	STD	Na	4000
4	3ppm		Standard	3	STD	Na	3000
5	4ppm		Standard	3	STD	Na	2500
6	5ppm		Standard	3	STD	Na	2000
7	10ppm		Standard	3	STD	Na	1000
8	20ppm		Standard	3	STD	Na	500
9	50ppm		Standard	3	STD	Na	200
10	80ppm		Standard	3	STD	Na	125
11	100ppm		Standard	3	STD	Na	100
12	133ppm		Standard	3	STD	Na	75
13	200ppm		Standard	3	STD	Na	50
14	500ppm		Standard	3	STD	Na	20

Figure: The SDX is capable of prescriptive dilution up to 5000

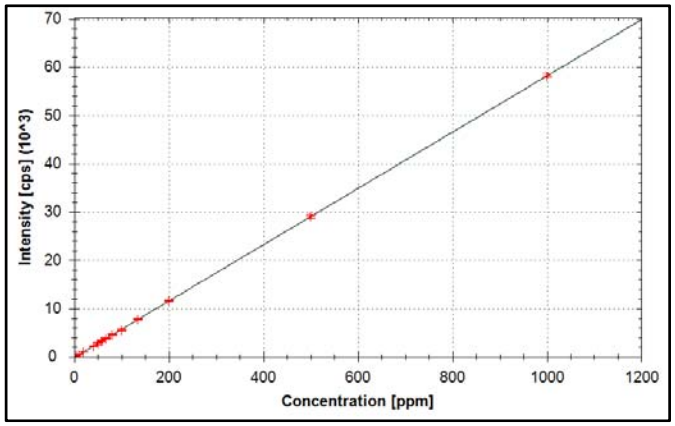


Figure: The SDX is capable of prescriptive dilution up to 5000

Label	Status	Rack	Vial	Dilution Fact	Autodilution Fact	Total Dilution Fact	Sample Type
Blank		Standard	3	1	1	1	UNKNOWN
Blank 1		Standard	3	1	1	1	BLK
STD 1		Standard	1	1	1000	1000	STD
STD 2		Standard	1	1	500	500	STD
STD 3		Standard	1	1	200	200	STD
STD 4		Standard	1	1	100	100	STD
STD 5		Standard	1	1	50	50	STD
STD 6		Standard	1	1	20	20	STD
STD 7		Standard	1	1	10	10	STD
Blank		Standard	3	1	1	1	UNKNOWN
TCD AGV-2		1	1	1000	10	10000	UNKNOWN

Figure: The SDX is capable of prescriptive dilution up to 5000

Intelligent Dilution

Enabling these two functions within Qtegra is as easy as clicking two boxes within the SDX autodilution tab. The user will then be able to define the limits to which the intelligent dilution parameters apply. First we will look at the intelligent dilution of samples that fall outside the pre-described range of the calibration line and how these can be applied to particular analytical methods.

Linear Dynamic Range

EPA Method 200.8 states that determined sample analyte concentrations that are 90% or more of the upper limit of the analyte LDR must be diluted with reagent water that has been acidified in the same manner as the calibration blank and reanalyzed. Therefore to comply with EPA method 200.8 we can set the limit % to 90 and the target % 50 and the SDX will intelligently dilute any sample with analyte concentrations at 90% or greater than the top standard back to the target % of 50% of the top standard value. The software choses the dilution factor based on the analyte with the highest concentration. All analytes that were already below the 90% limit % will not be reanalyzed as they are already within the defined limits.

Calibration Range

The USGS geo-standard AGV-2 previously prescriptively diluted by 10 was found to be over range and was intelligently diluted by a factor of 1408.455 giving a total dilution of 1408455. Intelligent Dilution is denoted by a line added into the sample list with the same sample name and a green plus mark in the status column.

Label	Status	Rack	Vial	Dilution Fact	Autodilution Fact	Total Dilution Fact	Sample Type
Blank		Standard	3	1	1	1	UNKNOWN
Blank 1		Standard	3	1	1	1	BLK
STD 1		Standard	1	1	1000	1000	STD
STD 2		Standard	1	1	500	500	STD
STD 3		Standard	1	1	200	200	STD
STD 4		Standard	1	1	100	100	STD
STD 5		Standard	1	1	50	50	STD
STD 6		Standard	1	1	20	20	STD
STD 7		Standard	1	1	10	10	STD
Blank		Standard	3	1	1	1	UNKNOWN
TCD AGV-2		1	1	1000	10	10000	UNKNOWN
TCD AGV-2		1	1	1000	1408.455	1408455	UNKNOWN
Blank		Standard	3	1	1	1	UNKNOWN

Figure:

Geostandards such as AGV-2 contain elements with concentrations from weight % down to ppb. When analyzing AGV-2 the top standard concertation was set at 100ppb. The ICPMS analysis showed the Al concentration to be at 8.4 ppm way beyond the 100% limit and also the Linear dynamic range of the instrument. QTEGRA calculated a dilution factor of 1408.455 in order to bring the concentration of Al back into range at the target of 0%.

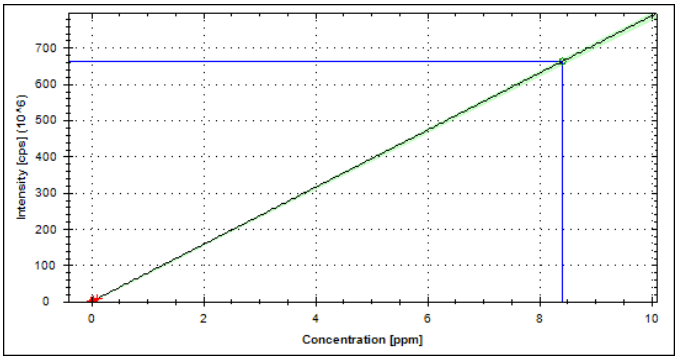


Figure: TCD AGV-2 All concentration values above linear dynamic range

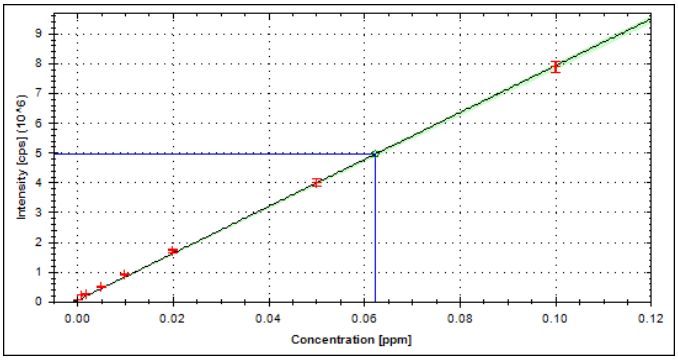


Figure: TCD AGV-2 + Intelligent dilution factor of 1408.455 applied

Internal Standard

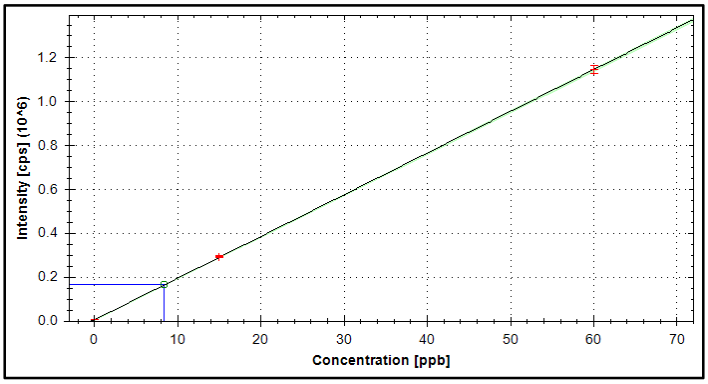
Suppression of internal standard can occur due to high dissolved solids content within samples. The intelligent dilution function for the internal standard will try to bring the internal standard back into a prescribed range by user defined:

1. Limits
2. Autodilition factor
3. Number of autodilution steps
4. Action if failure occurs

The intelligent dilution of the internal standard back into range is necessary as suppression of internal standard can occur due to high dissolved solids content within samples or other matrix effects suppressing or enhancing the intensity of the internal standard which needs to remain constant. The intelligent dilution function for the internal standard will try and bring the internal standard back into a pre-described range.

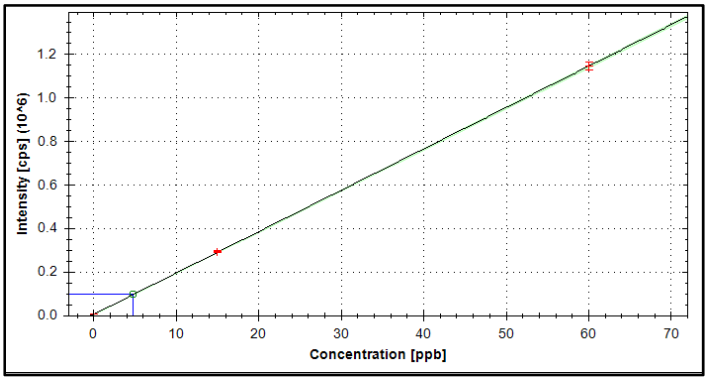
The user can define the auto dilution factor which will be used. Please note that the defined auto dilution factor will be added to any initial dilution factor prescriptively applied in order to increase the dilution factor. The user can also chose the action for the lab book if the internal standard fails to be brought back into range these actions can be wash and continue or abort the lab book.

In this example the concentration of Cu65 was calculated to be 8.1ppb however the software detected that the Y intensity had moved out of the prescribed range. The intelligent dilution of the sample was triggered, as the sample had already been prescriptively diluted by 20 the software applied a dilution factor of 40 to the sample. In the second plot you can see that the re calculated concentration value for Cu65 is now 4.9 ppb. However the software has now detected after the internal standard has been corrected that 51V 75AS and Pb208 are beyond the linear dynamic range value set in the calibration range part of the intelligent dilution settings



User comment: Intelligent Dilution (5/28/2017 6:38:45 PM)

Internal standard concentration out of range for: 89Y (KED)



User comment: Intelligent Dilution (5/28/2017 6:41:58 PM)

All internal standard concentrations in range.

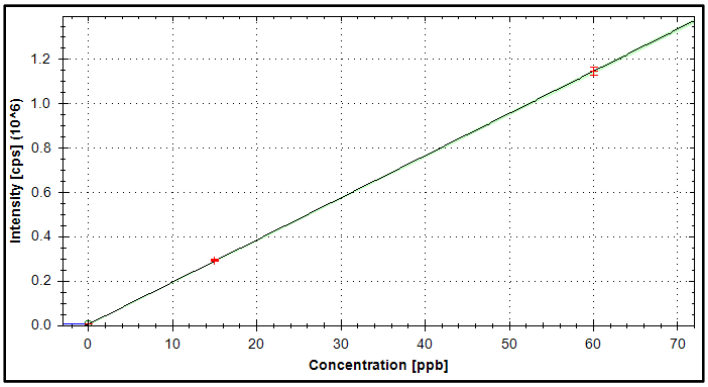
User comment: Intelligent Dilution (5/28/2017 6:41:58 PM)

Analyte concentration out of range for: 51V (KED), 75As (KED), 208Pb (KED)

User comment: Intelligent Dilution (5/28/2017 6:38:45 PM)

Measured with corrected dilution factor of 40.

The sample is now diluted by a factor of 145.388 which has brought all analytes into the linear dynamic range. The QTEGRA plug in logic dictates that the internal standard is brought back into the user defined range prior to carrying out an intelligent dilution due to analytes being outside the user defined limits on the calibration range.



User comment: Intelligent Dilution (5/28/2017 6:46:23 PM)

All analyte concentrations in range.

User comment: Intelligent Dilution (5/28/2017 6:41:58 PM)

Measured with corrected dilution factor of 145.388.

Traceability

The QTEGRA plug in for the SDX HPLD system enables the user to have full traceability of sample preparation.

As seen the USGS Geo-standard AGV-2 had a 1000x dilution associated with its initial digestion and preparation and then had a prescriptive dilution giving a total dilution of 10000. Therefore all auto dilutions are tracked within the software meaning that errors associated with noting information down is decreased.

Label	Status	Rack	Vial	Dilution Fact	Autodilution Fact	Total Dilution Fact	Sample Type
Blank		Standard	3	1	1	1	UNKNOWN
Blank 1		Standard	3	1	1	1	BLK
STD 1		Standard	1	1	1000	1000	STD
STD 2		Standard	1	1	500	500	STD
STD 3		Standard	1	1	200	200	STD
STD 4		Standard	1	1	100	100	STD
STD 5		Standard	1	1	50	50	STD
STD 6		Standard	1	1	20	20	STD
STD 7		Standard	1	1	10	10	STD
Blank		Standard	3	1	1	1	UNKNOWN
TCD AGV-2		1	1	1000	10	10000	UNKNOWN
TCD AGV-2		1	1	1000	1408.455	1408455	UNKNOWN
Blank		Standard	3	1	1	1	UNKNOWN

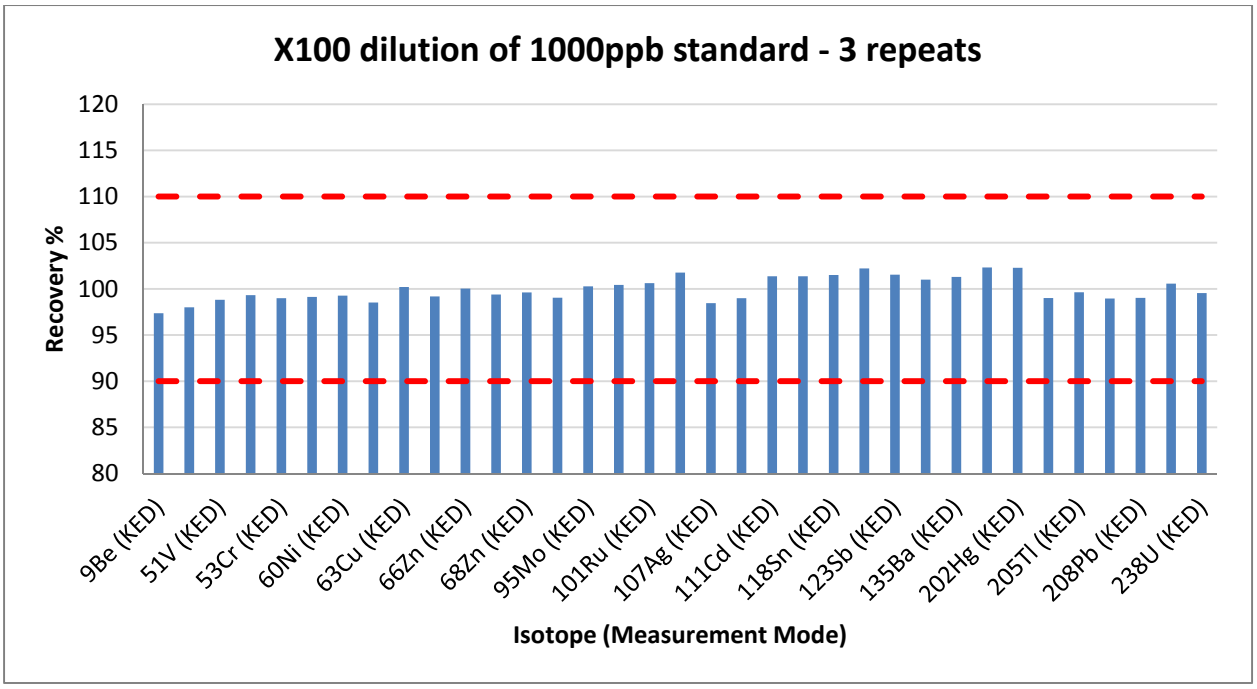
Figure: Full traceability of sample preparation digestion dilution and prescriptive dilution giving total dilution factor.

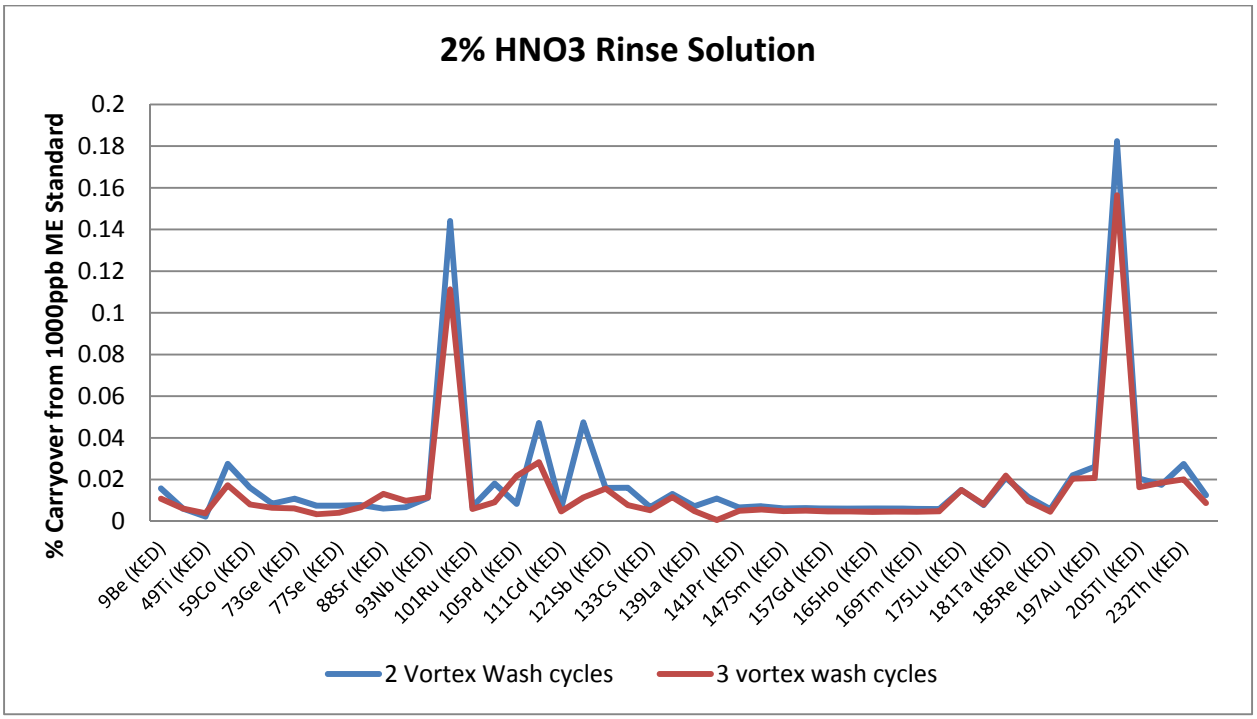
Label	Status	Rack	Vial	Dilution Fact	Autodilution Fact	Total Dilution Fact	Sample Type
Blank		Standard	3	1	1	1	UNKNOWN
Blank 1		Standard	3	1	1	1	BLK
STD 1		Standard	1	1	1000	1000	STD
STD 2		Standard	1	1	500	500	STD
STD 3		Standard	1	1	200	200	STD
STD 4		Standard	1	1	100	100	STD
STD 5		Standard	1	1	50	50	STD
STD 6		Standard	1	1	20	20	STD
STD 7		Standard	1	1	10	10	STD
Blank		Standard	3	1	1	1	UNKNOWN
TCD AGV-2		1	1	1000	10	10000	UNKNOWN
TCD AGV-2		1	1	1000	1408.455	1408455	UNKNOWN
Blank		Standard	3	1	1	1	UNKNOWN

Figure: Intelligent dilution factor is automatically applied to the total dilution factor.

Accuracy and Carryover

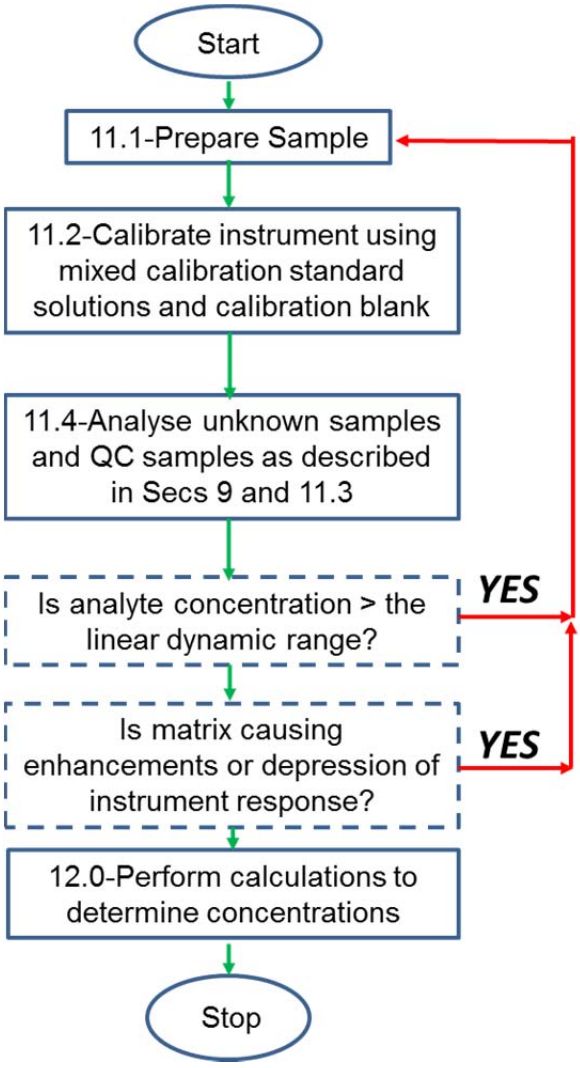
The accuracy of the SDX is demonstrated here by a plot of the recovery from a 100 x dilution of a 1000ppb multi element standard. The data is from 3 repeats of the same x100 dilution. The data demonstrates that the system is accurate to within 3% RSD.

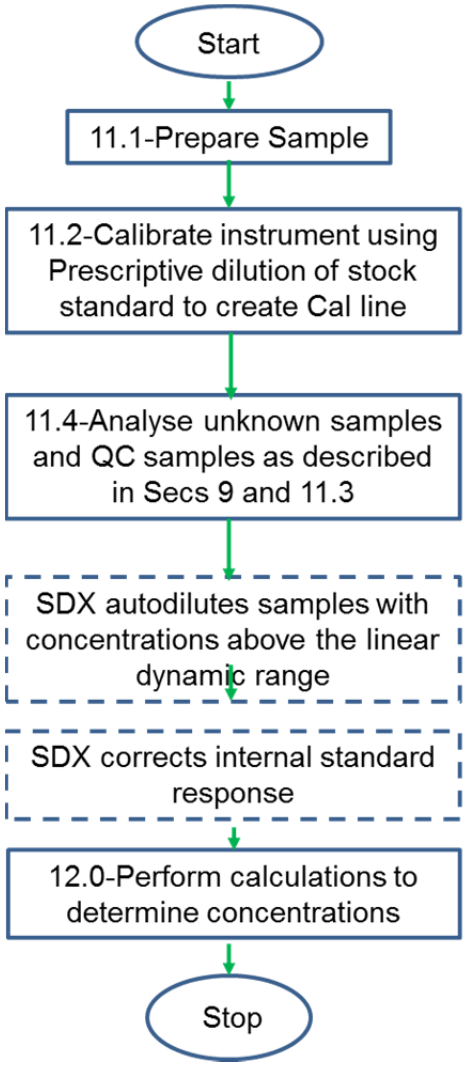




Method 200.8 – Manual vs. SDXHPLD

In the figure below we see the workflow of method 200.8 utilizing manual dilutions. The laboratory technician must first prepare the samples and then prepare the calibration standards and blank solution. Method 200.8 utilizes 6 different standard solutions due to chemical incompatibility within the solutions meaning a possible 18 different standard solution would need to be made for a four point calibration curve. Next the samples and QC samples are analysed. The method dictates that any analyte concentration is greater than the linear dynamic range then the sample need to be re diluted and analysed again. The method also states that if matrix causes enhancements or depression of the instrument response then the sample should be diluted and re-analysed. It is only after all samples pass these criteria that concentration values can be determined.





Teledyne CETAC Technologies
14306 Industrial Road
Omaha, NE 68144 USA
+1.402.733.2829
teledynecetac.com

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