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Application Note

Automating EPA Method 200.7 using the SDX$_{HPLD}$ High Performance Liquid Dilution System

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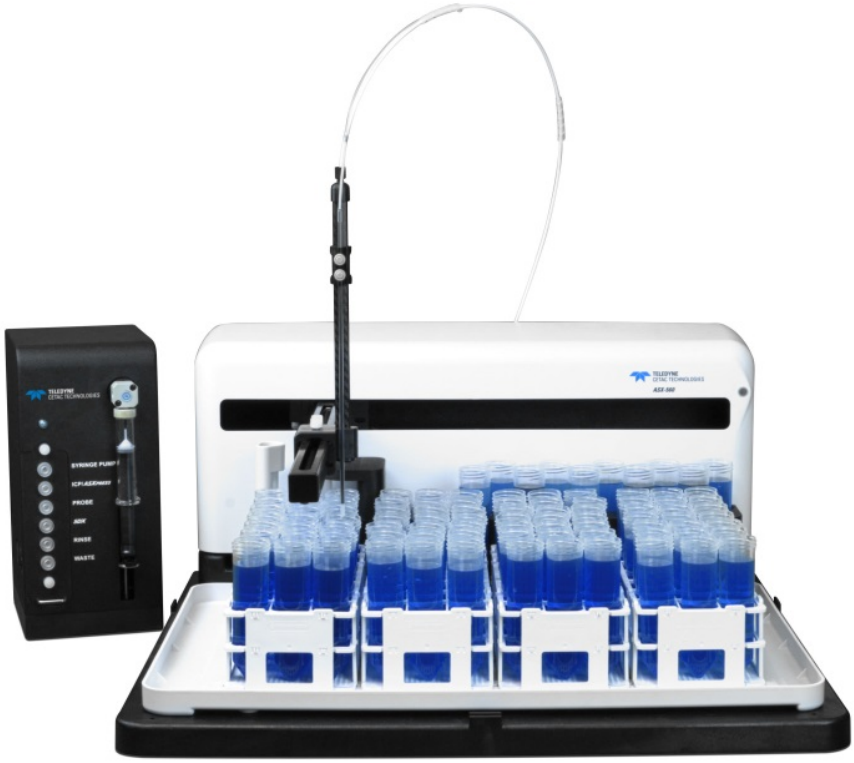


The SDX HPLD system combines the proven ASX-560 autosampler with a novel vortex mixing dilution accessory, enabling prescriptive and intelligent dilution of samples up to a factor of 5000X.

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 200.7 necessitates the need for large dilution factors.

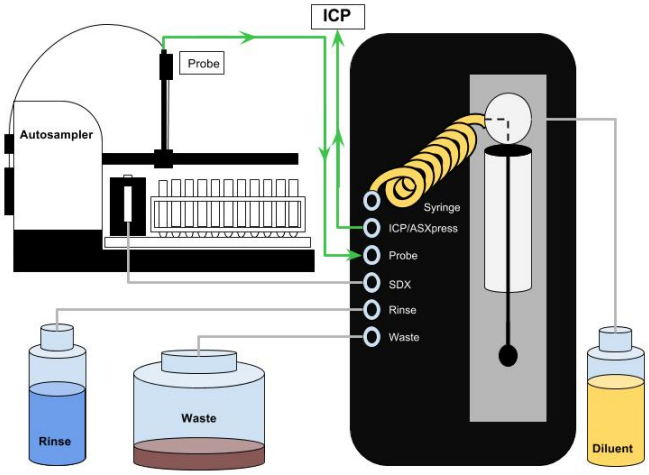
Functionality

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.

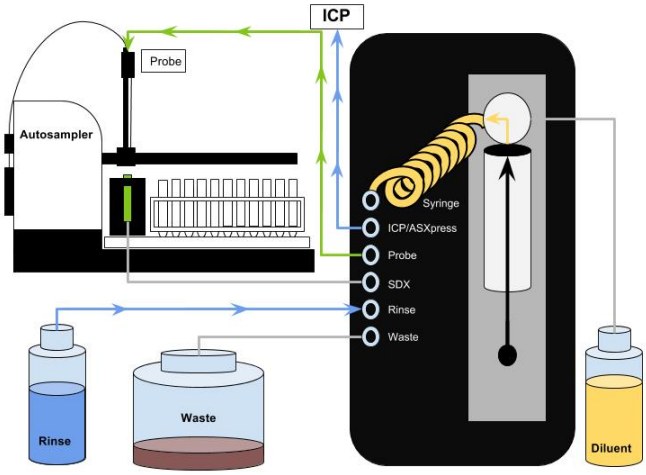
Normal Operation

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

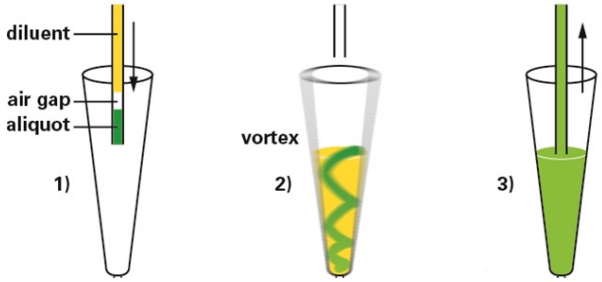


Dilution and Mixing

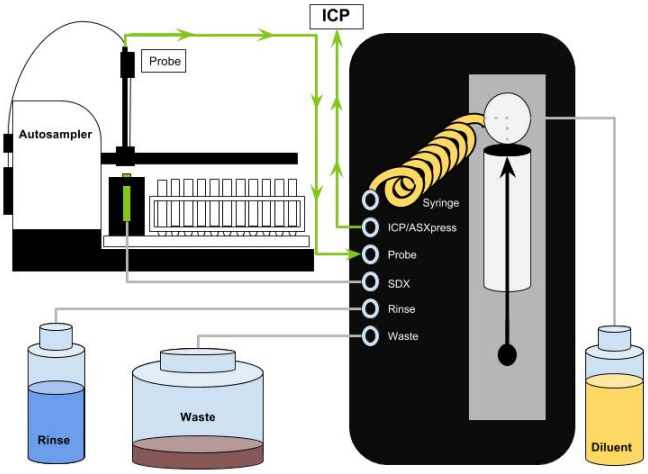
1. For a dilution, the sample probe is connected to a high resolution syringe pump for aliquot, air gap and diluent addition to the vortex mixing vessel.



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

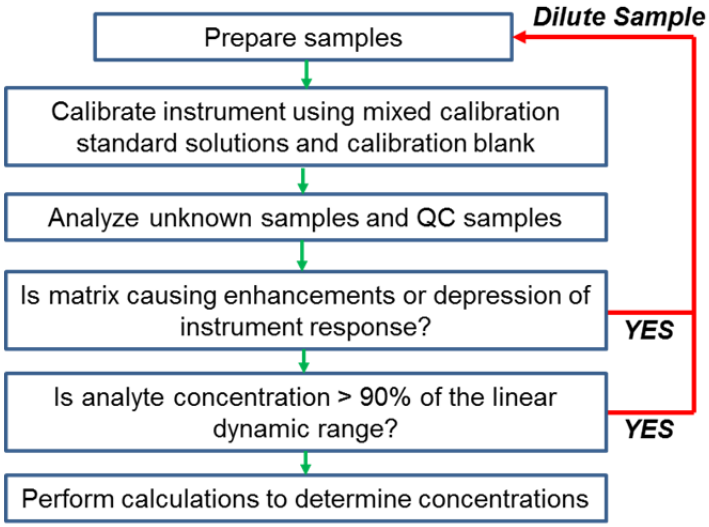


3. Sample uptake into the ICP-MS/ICP-OES can be either via loop loading with Sprint valve/*ASX*PRESS PLUS systems or via peristaltic pump.



EPA Method 200.7 Laboratory Workflow

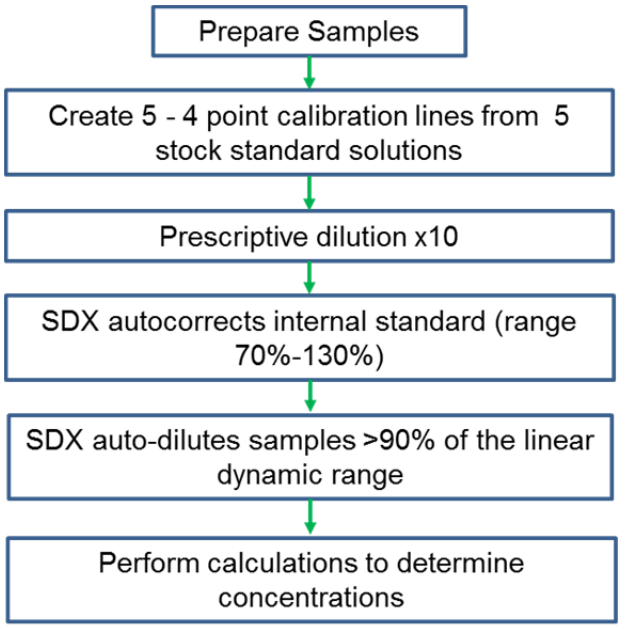
High throughput laboratories report up to 25% of samples per run requiring re-analysis due to samples being above the linear dynamic range or matrix effects causing suppression or enhancement to the internal standard response. This is a major cause of loss of lab productivity.



EPA Method 200.7 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 200.7

By utilizing the SDX HPLD to carry out EPA Method 200.7 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)

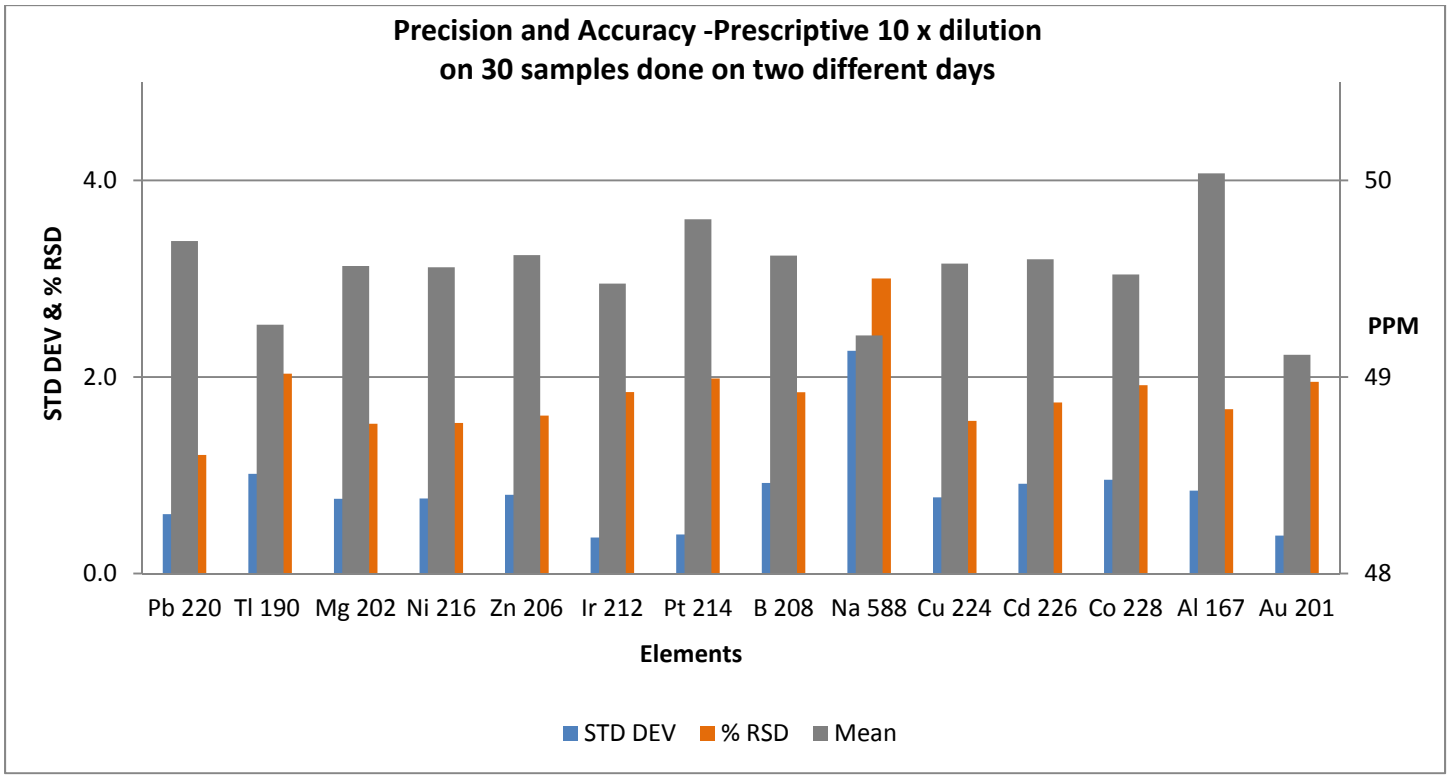
Element	Al	B	Ba	Be	Ca	Cr
LOD	0.9	1.95	3.9	0.072	0.015	0.3
LOQ	3	6.5	13	0.24	0.05	1

Element	Cu	Fe	K	Li	Mg	Mn
LOD	0.9	0.42	0.09	12.9	0.0036	0.12
LOQ	3	1.4	0.3	43	0.012	0.4

Element	Mo	Na	Sr	Zn
LOD	1.2	0.9	0.0003	2.1
LOQ	4	3	0.001	7

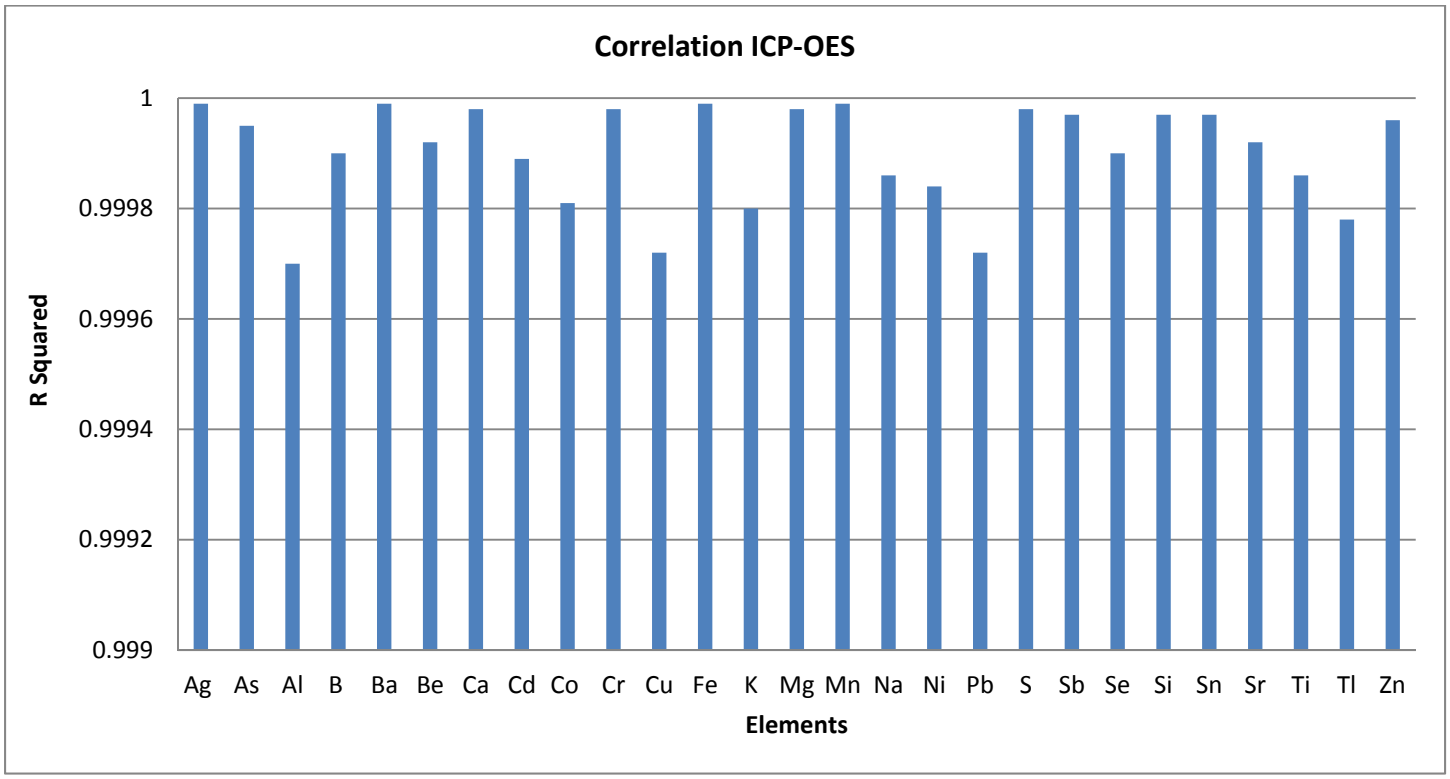
Accuracy and Precision

Here we plot 30 dilutions on two different days. 60 dilutions in total. 10 x dilution was performed on a 50 PPM standard.



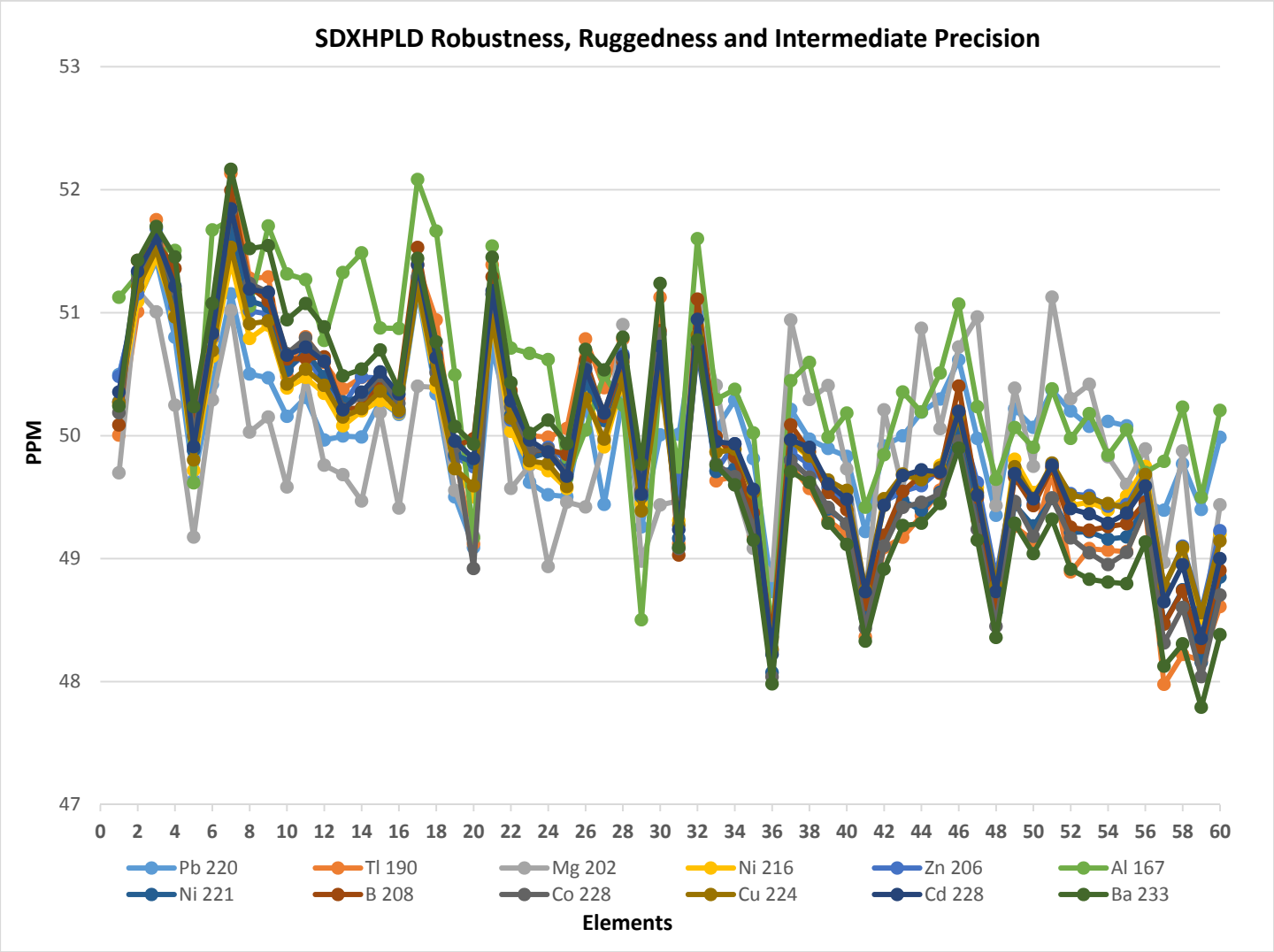
Correlation

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 on a iCAP 6500 series dual view system utilizing a 100ppm Multi Element standard. As you can see the majority of elements display greater than four 9 correlation with the exception of Na and Mercury which display around 0.9995 correlation.



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 of the future transferability of an analytical method. A 10x dilution was performed on a 50 ppm standard. Run in 30 replicates on two different days. With an identical SDX prepared curve. Intermediate precision is also satisfied here because the data differs by less than 10%.



Robust-Watts changed

Ruggedness-data run on day 2 with different (new peristaltic pump) tubing

Intermediate Precision- Data run on 2 different days

Specificity of Target Analyte

Specificity is the ability to quantify and identify target analytes in the presence of components which could or are expected to be present. The figure below shows that the certified lab preps their interference check standards (ICSA & ICSAB) in a dilute concentration in order to fit into their calibration curve. The ASX/SDX show results of higher concentrations of metals that are in the ICSAB going though intelligent dilution in order to fit into the calibration curve. Specificity is the ability to assess unequivocally the target analyte in the presence of components which may be expected to be present. Typically, these might include impurities, degradants, matrix, etc. This definition has the following implications:

	Certified Value with the value the certified lab reported	Al ASX/SDX
Blank	< MDL / 0.008	0.092
ICSA	500 ppm / 518	514
ICSAB	500 ppm / 513	499
200.7 MB	< MDL / 0.043	-0.109
200.7 LCS	2 ppm / 1.901	2.35
Unspike sample	10.306	12.293
200.7 MS	sample +2 ppm / 12.4	14.314
200.7 MSD	sample +2 ppm / 12.5	14.545
CCV recovery	106%	80%

	Certified Value with the value the certified lab reported	Be ASX/SDX
Blank	< MDL / -0.001	0.014
ICSA	< MDL / -0.001	0.094
ICSAB	0.5 ppm / 0.475	0.532
200.7 MB	< MDL / -0.001	-0.041
200.7 LCS	1 ppm / 0.954	0.985
Unspike sample	-0.001	0.008
200.7 MS	sample +1 ppm /0.9	1.02
200.7 MSD	sample +1 ppm / 0.908	1.04
CCV recovery	99%	96%

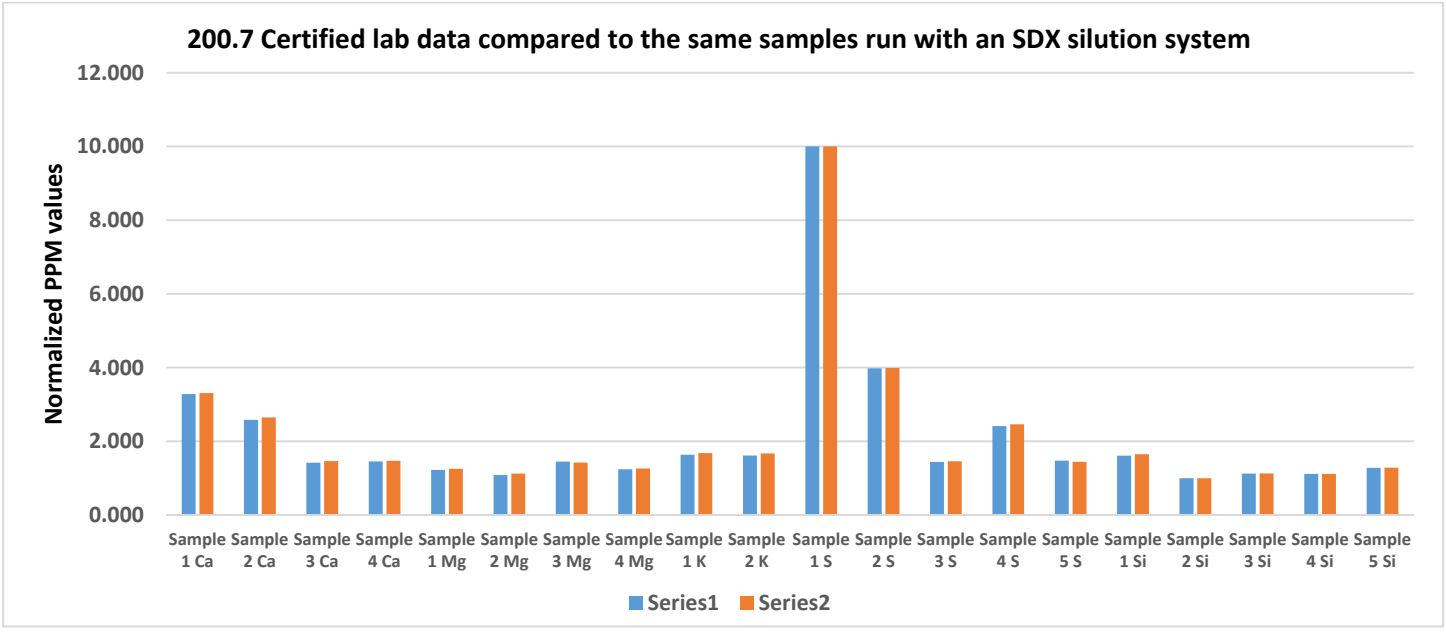
	Certified Value with the value the certified lab reported	Ag ASX/SDX
Blank	< MDL / 0.001	0.004
ICSA	0 ppm / 0	0.004
ICSAB	1.0 ppm / 1.013	1.087
200.7 MB	< MDL / 0.002	0.007
200.7 LCS	1 ppm / 0.858	1.056
Unspike sample	0.001	0.001
200.7 MS	sample +1 ppm / 0.919	1.052
200.7 MSD	sample +1 ppm / 0.992	1.045
CCV recovery	102%	105%

	Certified Value with the value the certified lab reported	Mg ASX/SDX
Blank	< MDL / 0.04	-0.178
ICSA	500 ppm / 508	519
ICSAB	500 ppm / 505	521
200.7 MB	< MDL / 0.004	-0.055
200.7 LCS	20 ppm / 20.047	23.195
Unspike sample	8.478	10.077
200.7 MS	sample +20 ppm / 27.44	32.27
200.7 MSD	sample +20 ppm / 27.71	32.99
CCV recovery	105%	96%

Figure: QC results from a 200.7 certified lab vs CETAC SDX$_{HPLD}$

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 200.7 lab. The samples in red were reported by SDX intelligent dilution. The samples in blue are from the EPA certified lab running 200.7.



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

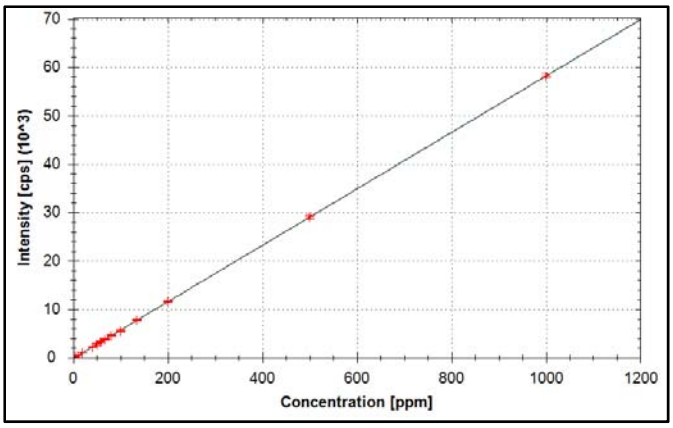


Figure: The SDX is capable of prescriptive dilution up to 5000

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 200.7 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 200.7 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%.

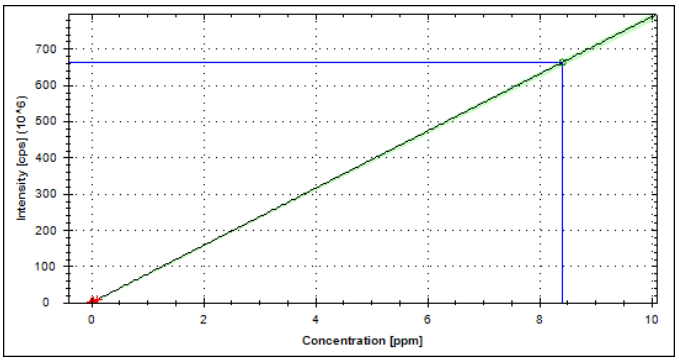


Figure: TCD AGV-2 All concentration values above linear dynamic range

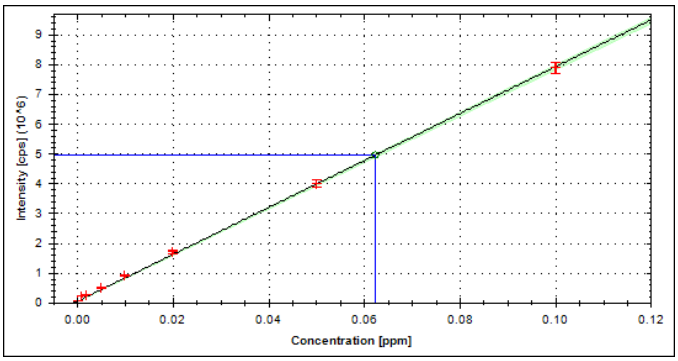


Figure: TCD AGV-2 + Intelligent dilution factor of 1408.455 applied

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.

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.

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