# Dissolved Oxygen Instrument Commissioning

The two new Dissolved Oxygen instruments purchased from SCRIPPS required testing to ensure they generate the same measurements as our existing instrument.

The new instruments are much newer than the existing Hobart and RV Investigator instruments. The dosimats are the newest versions - 876 series – which require a different software version. LVO2 software to work with the new dosimats has the dosimats model trailing, i.e. LVO2\_876.

In this report the instruments are referred to as New A, New B and Old.

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# One Page Summary

The new dissolved oxygen instruments perform just as well as the old instrument, these experiments even found that the new instruments have potentially better measurement precision than the old. Instrument New B (marked B on right side inside box) has been installed and setup in the Hydrochemistry laboratory.

More testing is required to tune in the titration parameters as each sample can take roughly 30 seconds longer than on the old instrument. This is not an issue in general usage – but would become frustrating (and cumulative, very time consuming) on large oceanographic voyages.

In these series of experiments the focus was on ensuring the new dissolved oxygen instruments could perform as well as the existing instrument and be suitable as replacements aboard RV Investigator. For the purposes of this investigation, a bigger focus was put upon the precision of measurements, rather than the exact accuracy.

To address any significant differences between instruments, most variables were attempted to be accounted for.

* Same temperature and air pressure environment
* Thermistors calibrated to same reference
* Burettes calibrated and volumes input to software
* Instruments standardised using same Potassium Iodate and Dosimat

This meant the accuracy between instruments was often statistically indifferent, though there were 2 cases where instrument New A was very slightly offset from the two other instruments. This offset equated to approximately 0.3% (<0.5µM) in both instances.

In terms of precision, instrument New A had the tightest groupings of data when the cross experiment meta-analysis was completed. It was followed by instrument new B, with the old instrument having the worst precision across all experiments. However, these differences were statistically insignificant (p=0.80), perhaps likely due to the small sample size of standard deviations (n=5).

# Methods

The dissolved oxygen instruments were setup in the wet/clean laboratory on RV Investigator main deck.

# Results

## Experiments Summary

|  |  |
| --- | --- |
| Experiment Overview | Instruments Tested |
| 3.1 | Measurement of an independently dispensed Iodate standard as a sample | New A, New B, Old |
| 3.2 | Repeated measurements of deep sample replicates: 1 | New A, New B, Old |
| 3.3 | Repeated measurements of atmospheric sample replicates | New A, New B, Old |
| 3.4 | Repeated measurements of atmospheric sample replicates | New B |
| 3.5 | Water Profile Comparison | New A, Old |
| 3.6 | Repeated measurements of deep sample replicates: 2 | New A, New B, Old |

## Independent Iodate Standards

This section 3.1 includes results from the measurement of independently dispensed Potassium Iodate standards. Standards were dispensed from a separate 10mL Dosimat that was calibrated prior to the voyage. The Dosimat also used a different batch of Potassium Iodate to independently verify the Thiosulfate normality.

### Iodate Standards across Instruments Boxplot

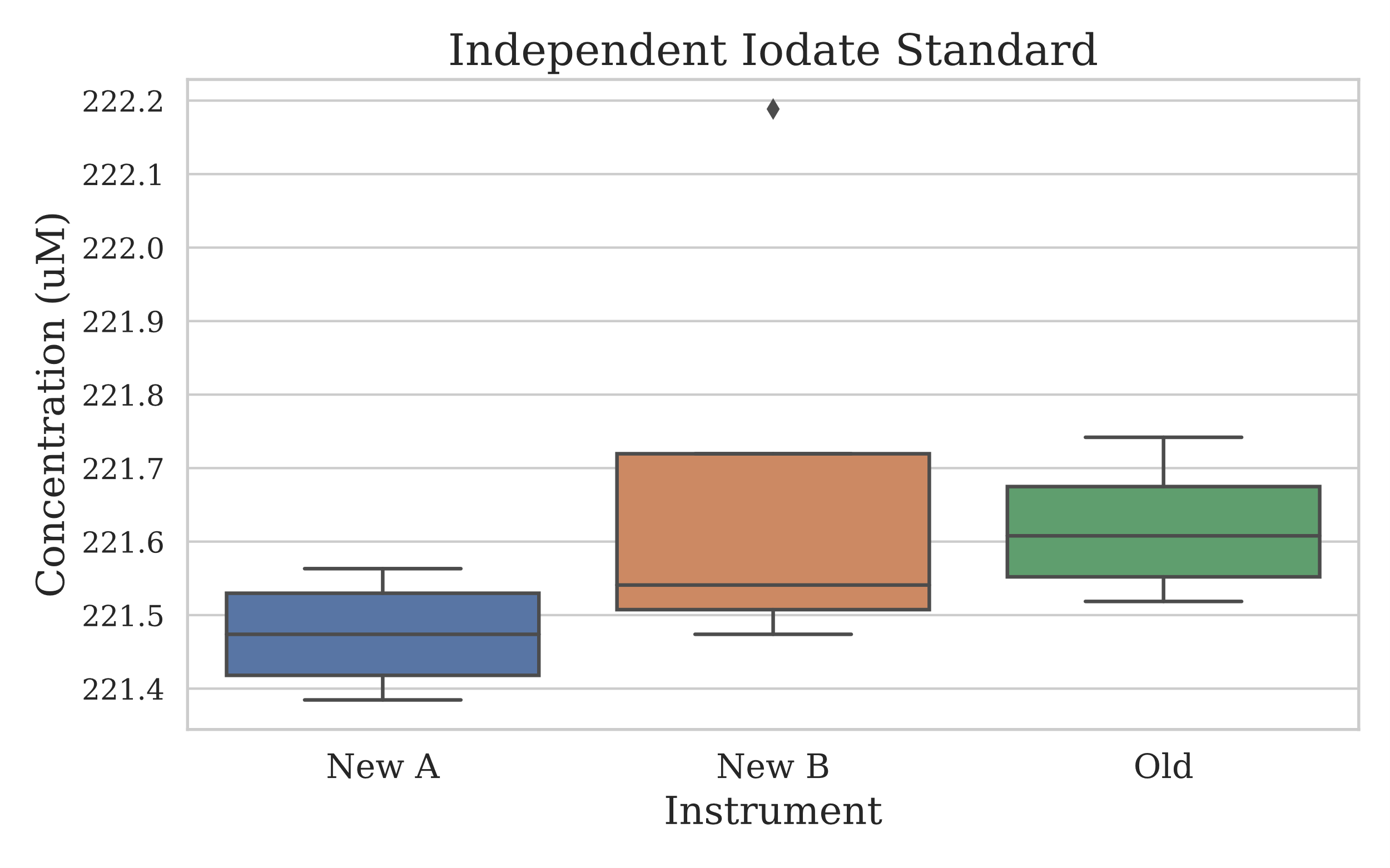


Figure 1.1.1: Boxplot style chart depicting the distribution of the independently dispensed Potassium Iodate standards measured by each instrument. Important to note that there was only 4 measurements made on each instruments.

### Iodate Standards Descriptive Statistics

|  |  |  |  |
| --- | --- | --- | --- |
|  | New A | New B | Old |
| Mean | 221.4739 | 221.6861 | 221.6191 |
| Median | 221.4739 | 221.5409 | 221.6079 |
| Standard Deviation | 0.0815 | 0.3369 | 0.0990 |
| % RSD | 0.037% | 0.152% | 0.045% |
| n | 4 | 4 | 4 |

Table 1.1.2: Basic descriptive statistics of the independently dispensed Potassium Iodate standards.

## Repeated Deep Sample Measurement: 1

Results section 3.2 pertains to the measurement of samples collected on deployment 1 from a depth of 1000 metres. Six sample replicates were taken from Niskins RP 3 to 7. For the first sub-section of this experiment, the 6 replicates from each Niskin were assigned to one instrument. For the second sub-section of this experiment, two replicates from each Niskin was measured by each instrument.



### Samples from One Niskin per Instrument

For each instrument tested, the samples were collected from a single Niskin. See table below for a tabulated view.

|  |  |  |  |
| --- | --- | --- | --- |
| Instrument | DEPLOYMENT | Niskin (RP) | Replicates |
| New A | 1 | 4 | 6 |
| New B | 1 | 7 | 6 |
| Old | 1 | 3 | 6 |

Table 1.2.1: Each instrument measured 6 replicate samples from a single niskin, the rosette position of the niskin is shown. Each bottle was fired sequentially, one after the other as quickly as possible at a depth of 1000 meters.

#### Samples from One Niskin Boxplot

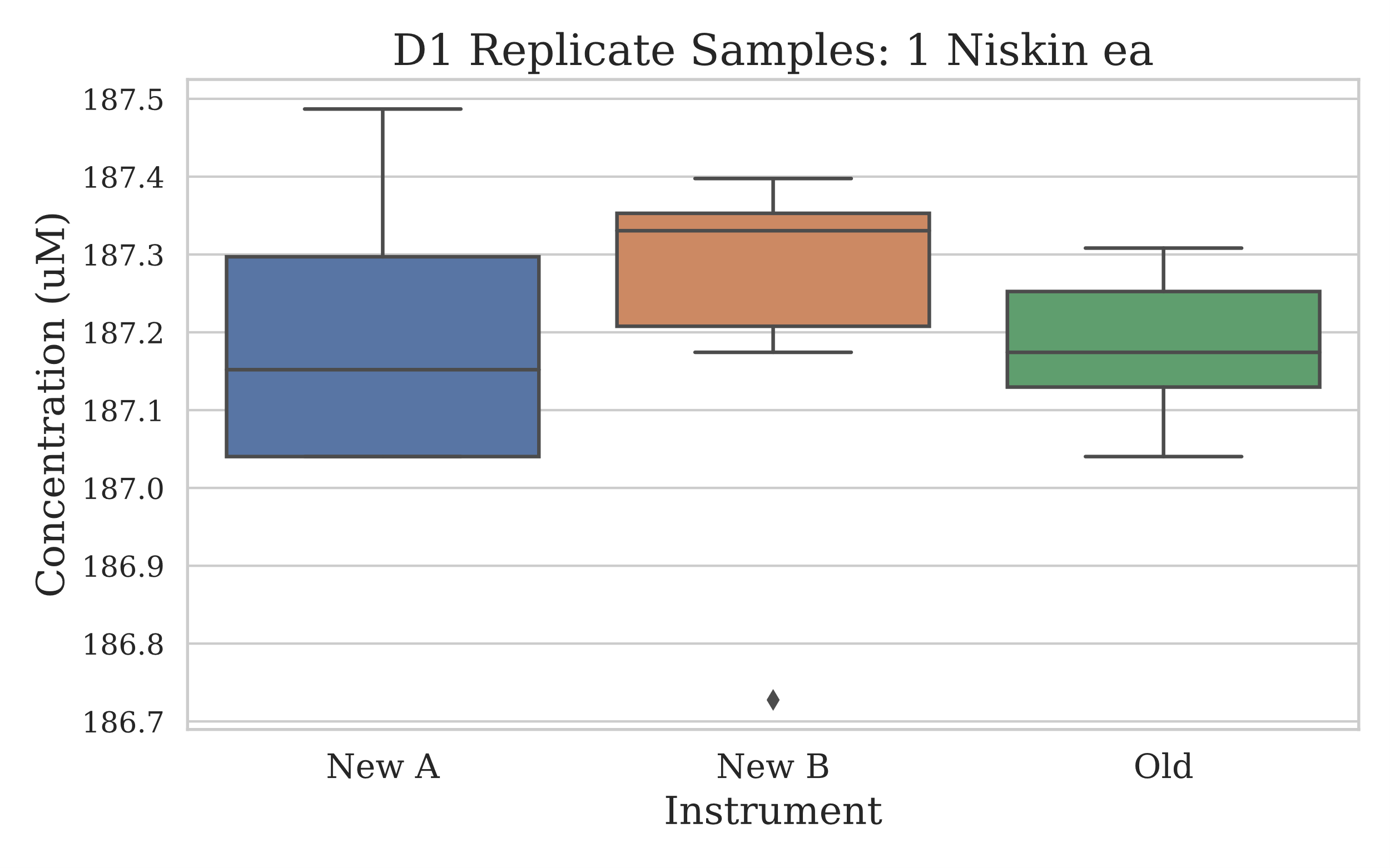


Figure 1.2.1.1: Boxplot style chart displaying the distribution of measurements for the sample replicates from each instrument.

#### Descriptive Statistics

|  |  |  |  |
| --- | --- | --- | --- |
|  | New A | New B | Old |
| Mean (uM) | 187.1966 | 187.2189 | 187.1817 |
| Median (uM) | 187.1520 | 187.3306 | 187.1743 |
| Standard Deviation | 0.1868 | 0.2526 | 0.0995 |
| % RSD | 0.100% | 0.135% | 0.053% |
| n | 6 | 6 | 6 |

Table 1.2.1.2: The basic descriptive statistics for the deep deployment sample replicates.

#### T-Test Comparison of Means

|  |  |  |
| --- | --- | --- |
| Comparison | P-Value | Significant Difference |
| New A to Old | 0.866 | No |
| New B to Old | 0.744 | No |

### Samples from Two Niskins for all Instruments

The samples to test all instruments were collected from two Niskins, this resulted in each instrument having 2 samples from each niskin – as 6 samples were collected from either Niskin.

#### Sample from Shared Niskins Boxplot

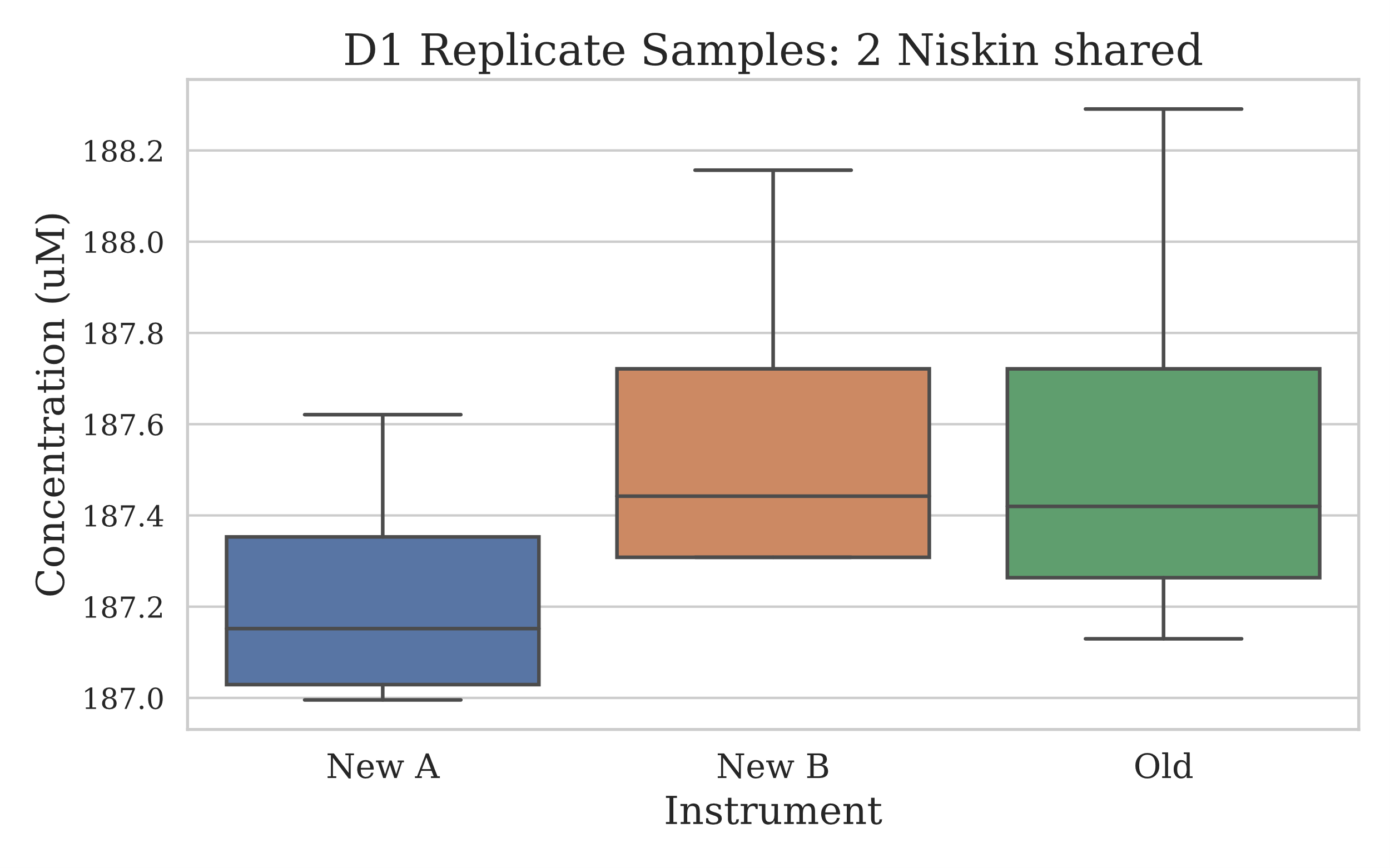


Figure 3.2.2.1: Depicted is a boxplot style chart where the samples measured are from 2 niskins and the replicates split between the 3 instruments. Each instrument made 4 measurements from the replicates pool.

#### Descriptive Statistics

|  |  |  |  |
| --- | --- | --- | --- |
|  | New A | New B | Old |
| Mean (uM) | 187.2301 | 187.5874 | 187.5650 |
| Median (uM) | 187.152 | 187.4422 | 187.4199 |
| Standard Deviation | 0.2856 | 0.4001 | 0.5110 |
| % RSD | 0.153% | 0.213% | 0.272% |
| n | 4 | 4 | 4 |

Table 3.2.2.2: Basic descriptive statistics of the shared deep water sample replicates.

## Atmospheric Saturated Sample: All Instruments

The results shown in this section, 3.3, were generated from the measurement of samples collected off the saturated oxygen rig. The rig was kept in the Hydrochemistry laboratory, where it equilibrated close to 21.5°C. Previous installation of the pressure monitor in the laboratory was used to get the air pressure at the time of sample collection. Both instances of sample collection, 12 samples were taken.

### Atmospheric Saturated Sample Boxplot (auto-scale)

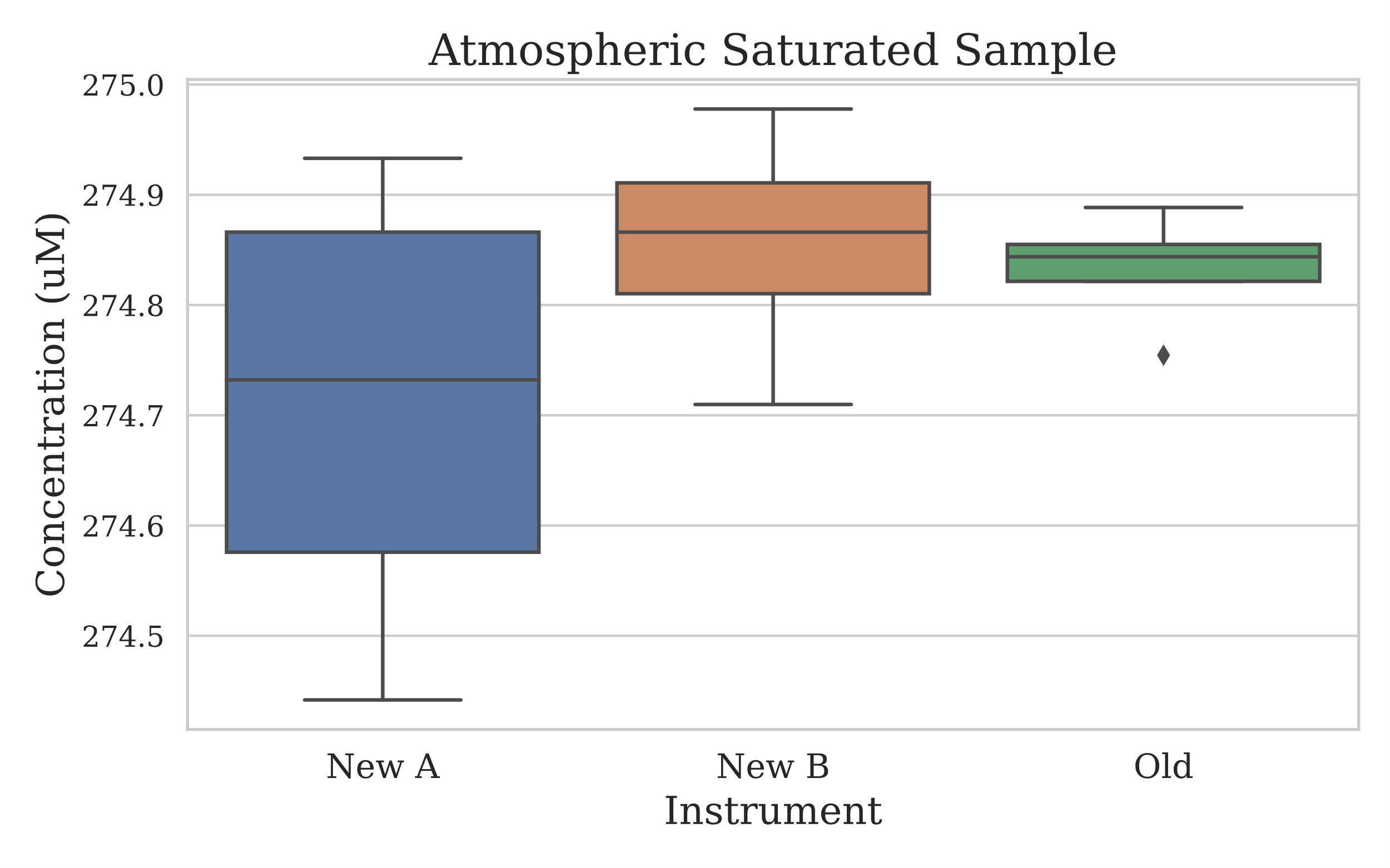


Figure 3.3.1: Boxplot style chart with the measurements made on the oxygen saturated samples created using the new rig. 12 samples in total were collected for this section, with each instrument analysing 4 of these.

### Atmospheric Saturated Sample Boxplot (QC Control Lines)

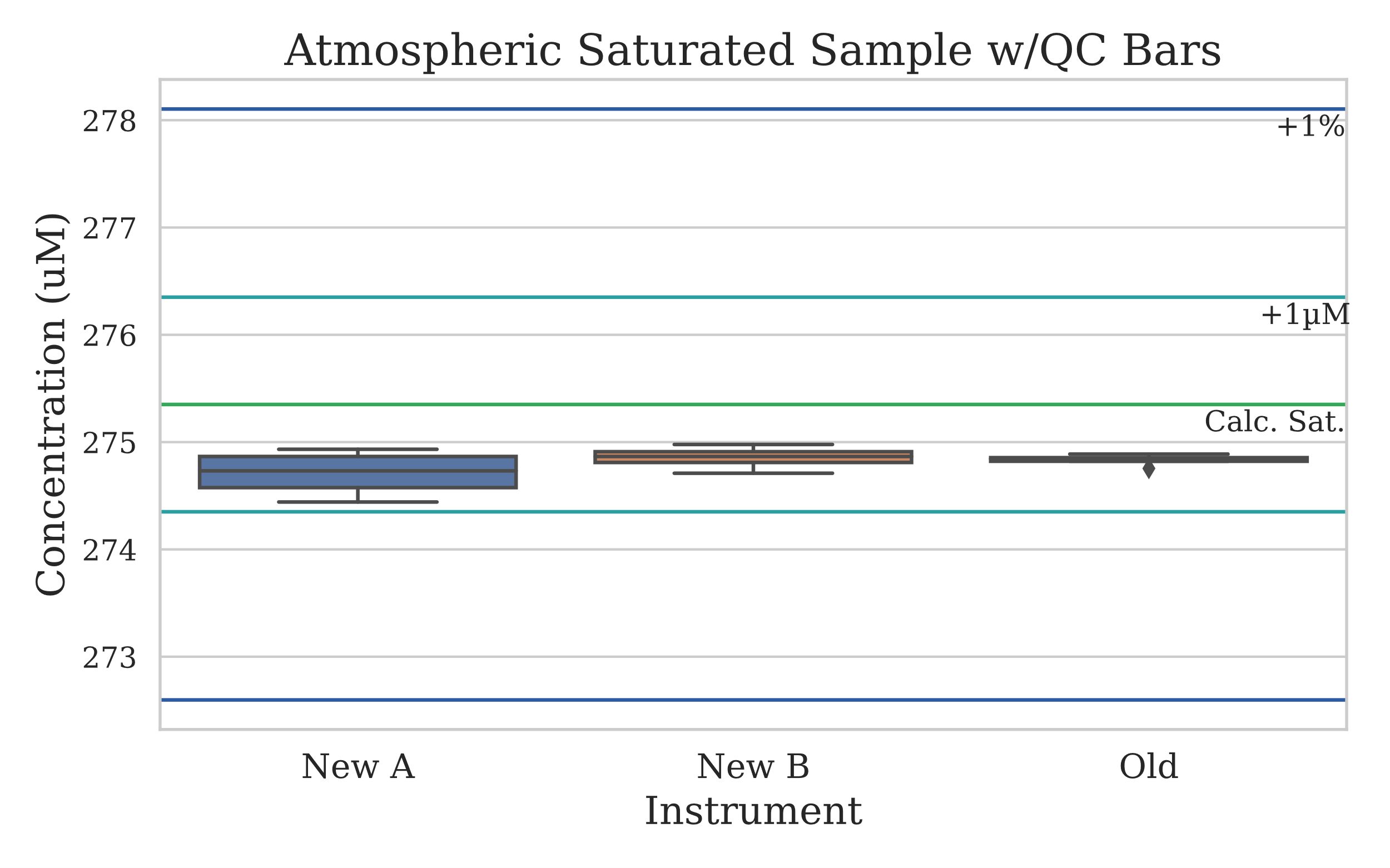


Figure 3.3.2: Boxplot of the same results from figure 3.3.1, however now depicted with quality control lines which show the theoretical oxygen saturation concentration (green), the saturated concentration ± 1µM (cyan) and the saturated concentration ± 1% of the concentration (blue).

### Descriptive Statistics

|  |  |  |  |
| --- | --- | --- | --- |
|  | New A | New B | Old |
| Mean (uM) | 274.7098 | 274.8550 | 274.8327 |
| Median (uM) | 274.7322 | 274.8662 | 274.8438 |
| Standard Deviation | 0.2218 | 0.1116 | 0.0562 |
| % RSD | 0.081% | 0.041% | 0.020% |
| n | 4 | 4 | 4 |

Table 3.3.3: Basic descriptive statistics of the saturated oxygen measurements.

## Atmospheric Saturated Sample: One Instrument

This section includes the results from the repeated measurement of saturated oxygen samples collected off of the rig. Samples were measured on instrument New B, this was 12 measurements.

### Atmospheric Saturated Sample: Instrument New B (auto-scale)

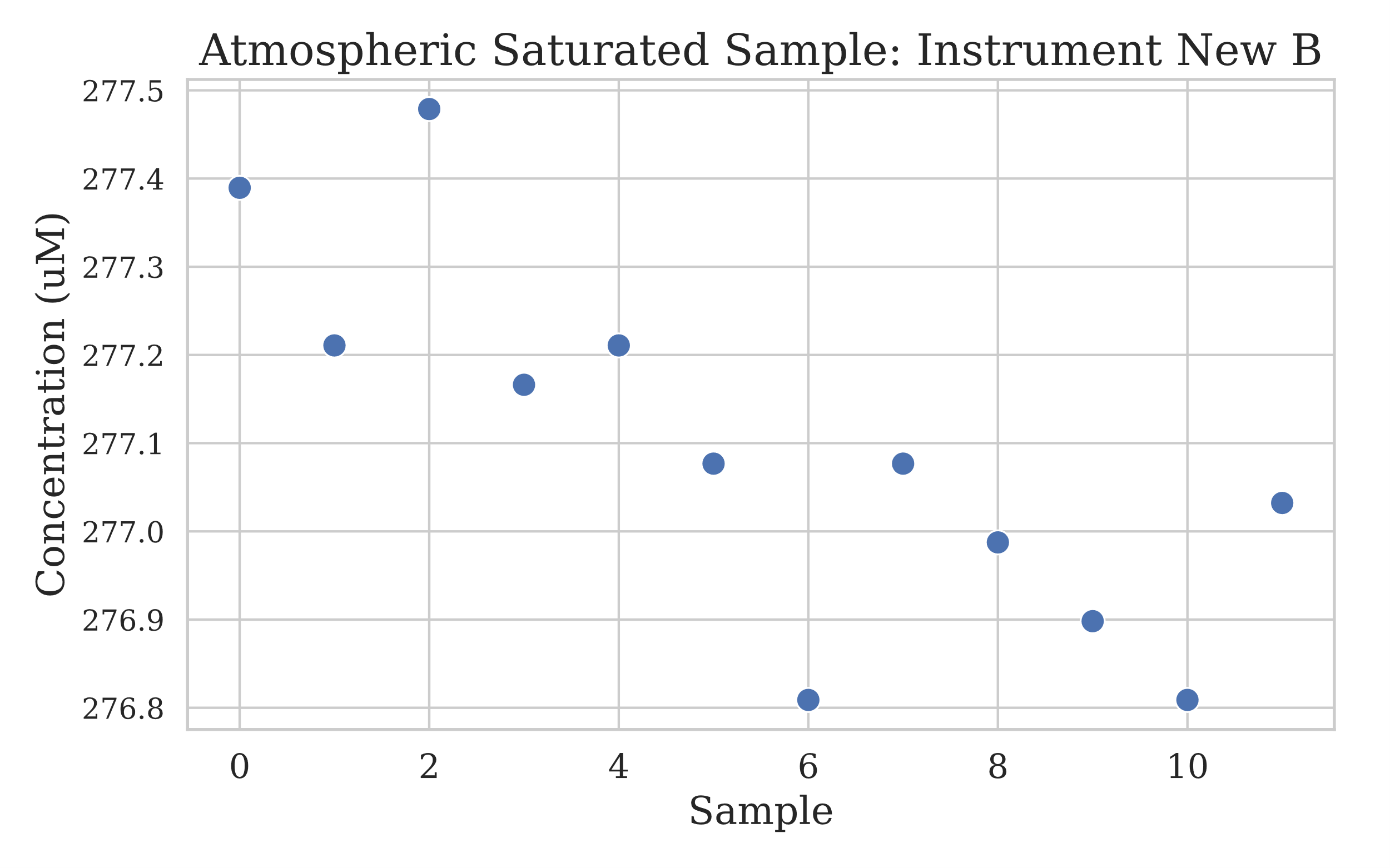


Figure 3.4.1: Scatter plot of the measurements made by instrument New B on a second set of 12 saturated oxygen atmospheric samples. The x axis is sample number in order of collection, y axis is concentration.

### Atmospheric Saturated Sample: Instrument New B (auto-scale)

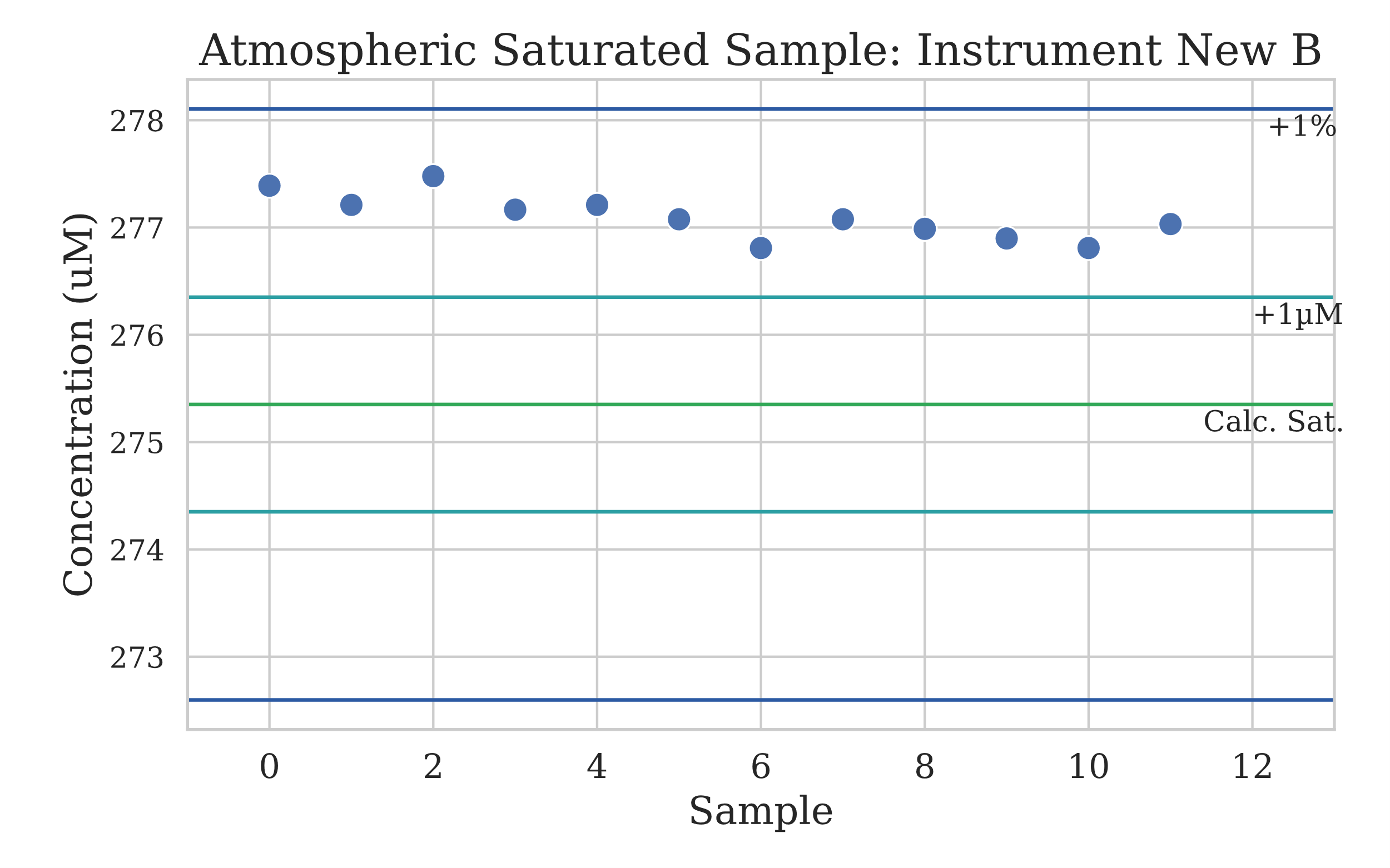


Figure 3.4.2: This scatter plot is like figure 3.4.1, however it includes quality control lines which show the theoretical oxygen saturation concentration (green), the saturated concentration ± 1µM (cyan) and the saturated concentration ± 1% of the concentration (blue).

### Atmospheric Saturated Sample: Instrument New B Boxplot (QC Control Limits)

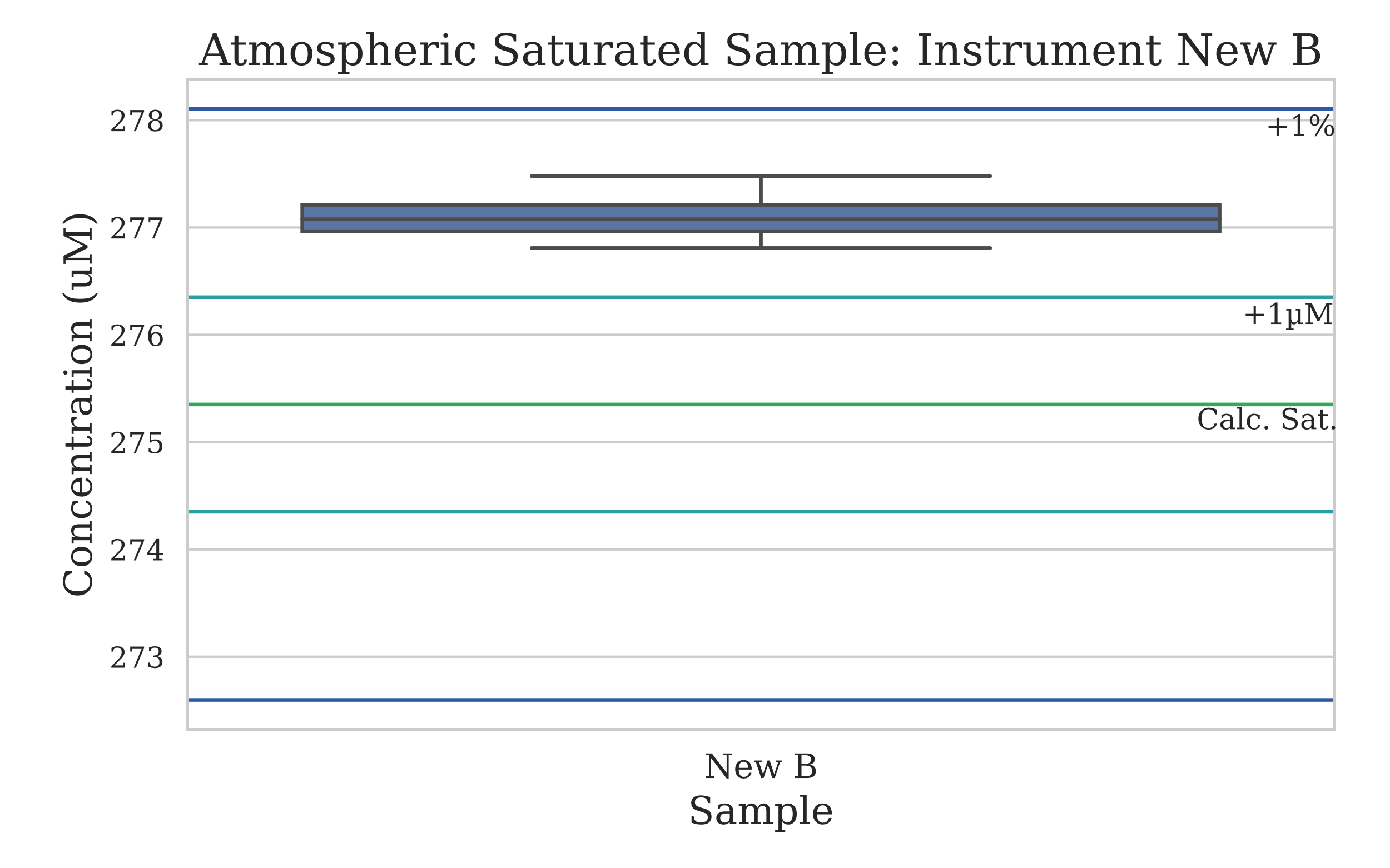


Figure 3.4.3: Very similar to figure 3.4.2, however depicted in a boxplot style to match the analysis completed on the other experiments.

## Water Profile Comparison

Duplicate samples were collected from a deployment that was used to go throughout the entire water column. Each duplicate sample was split between two instruments, New A and Old. There was also niskin replicates as every depth, most depths contained triplicate firings. These samples were collected on deployment 1.

### Water Profile Plot

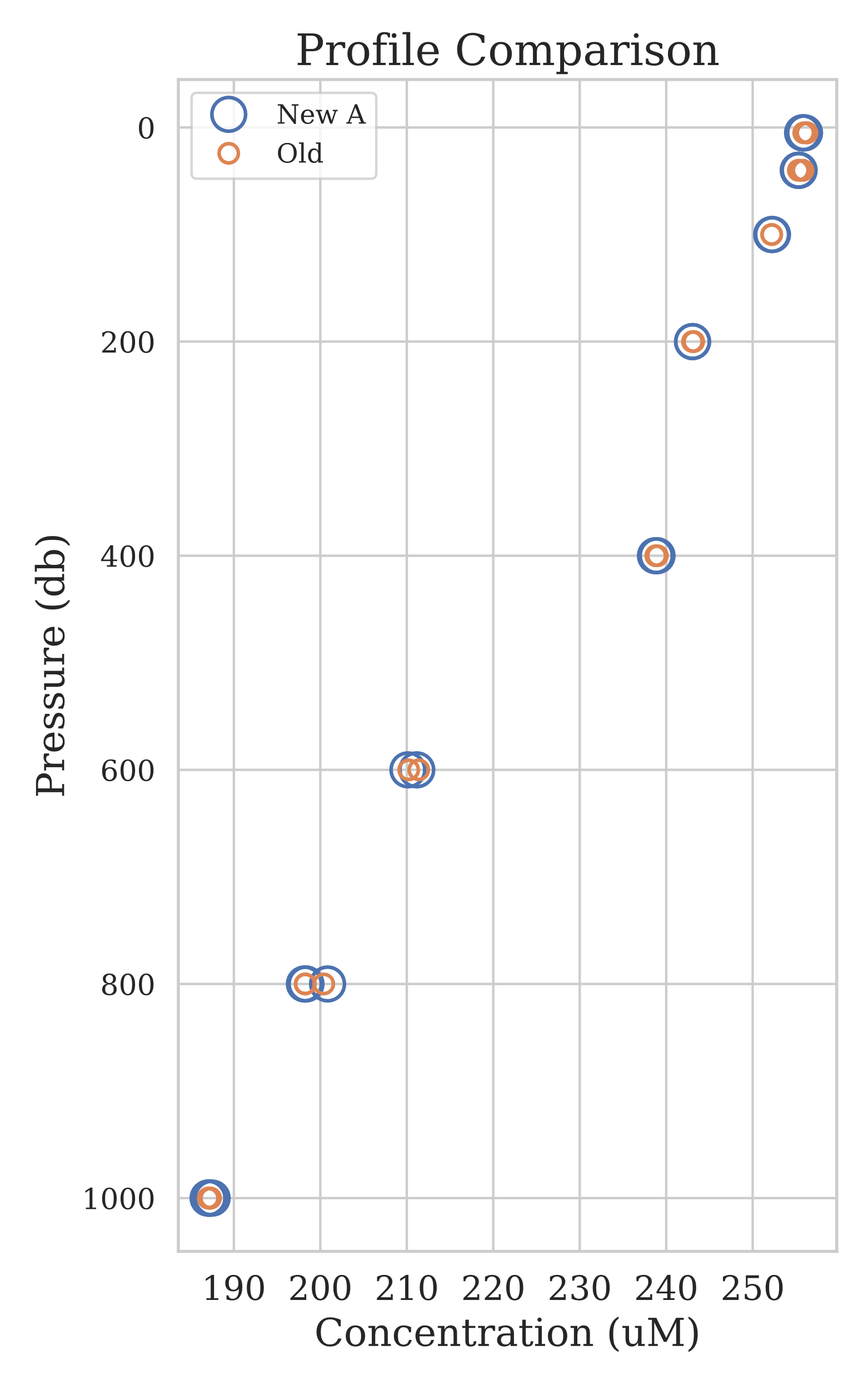


Figure 3.5.1: Profile plot where the y axis is pressure (reversed, 0 at top), x axis is concentration. The different instrument measurements are depicted by the circle colours and size, small orange circles are Old instrument and bigger blue circles are the New A instrument.



### T-Test Comparison of Means at specific depths

|  |  |  |
| --- | --- | --- |
| Depth | P-Value | Significant Difference |
| 5 | 0.10 | No |
| 40 | 0.30 | No |
| 800 | 0.90 | No |
| 1000 | 0.86 | No |

Table 3.5.2: T-Tests were completed on the depths where triplicate firing occurred. This test is used to ascertain if there is a difference in the means of the two groups (in this case Instruments). None of the tests produced a significant result for the samples throughout the water column.

## Repeated Deep Sample Measurement: 2

Deployment 2 involved firing all Niskin bottles at the bottom depth of 1000 meters. A dissolved oxygen sample was then taken from each niskin, this resulted in each instrument measuring 8 samples of the total 24 replicates.

### Deployment 2 Replicates Boxplot

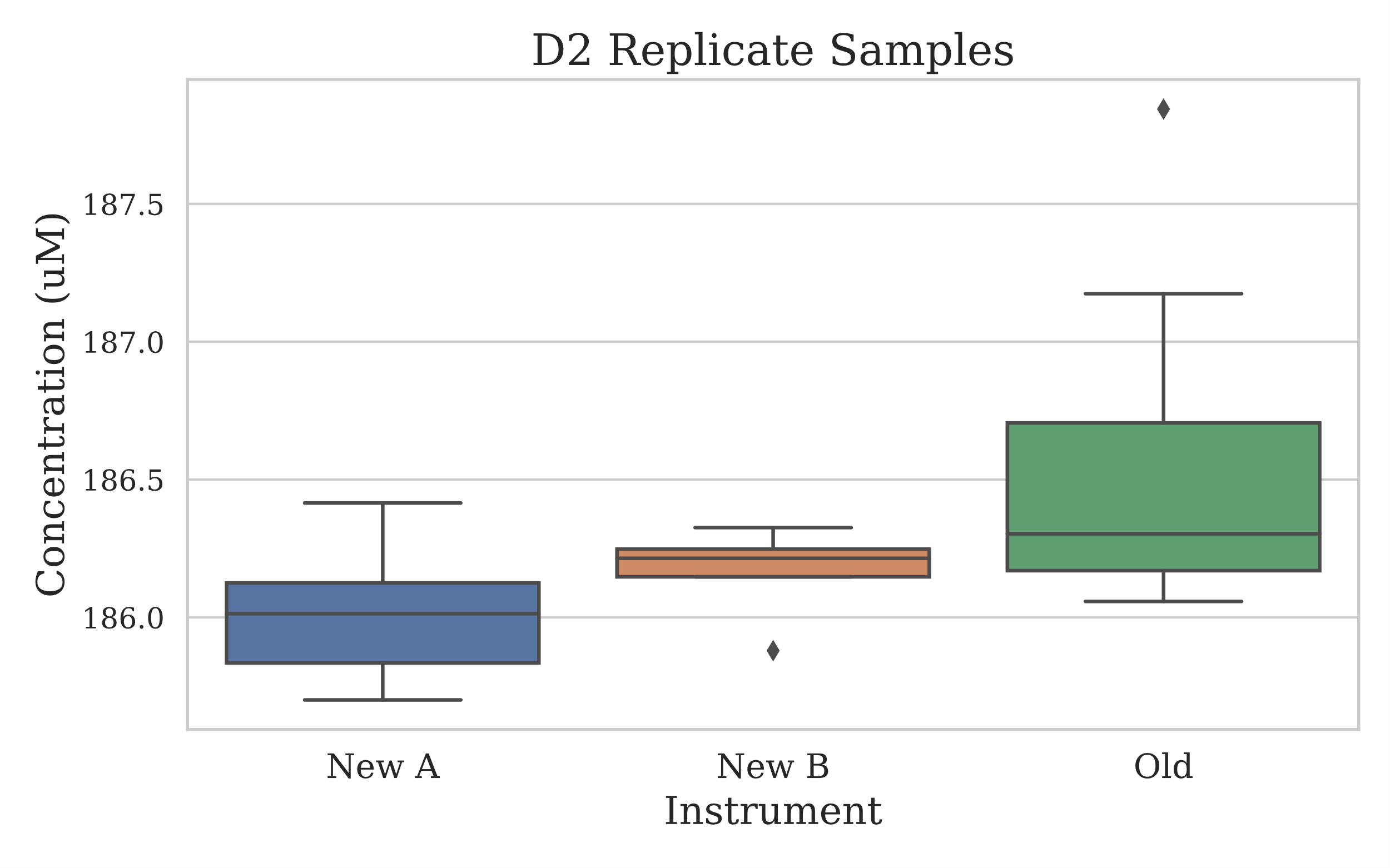


Figure 3.6.1: Boxplot style chart of the measurements made on replicates taken from deployment 2. The replicates were produced by firing every Niskin bottle at 1000 meters, a sample was then taken from each bottle. Each instrument then analysed 8 samples.

### T-Test Comparison of Means

|  |  |  |
| --- | --- | --- |
| Test Comparison | P-Value | Significant Difference |
| New A to Old | 0.04 | Yes |
| New B to Old | 0.11 | No |

Table 3.6.2: T-Test comparison of the deployment 2 replicates.

# Discussion

# Appendix

## CTD deployment locations