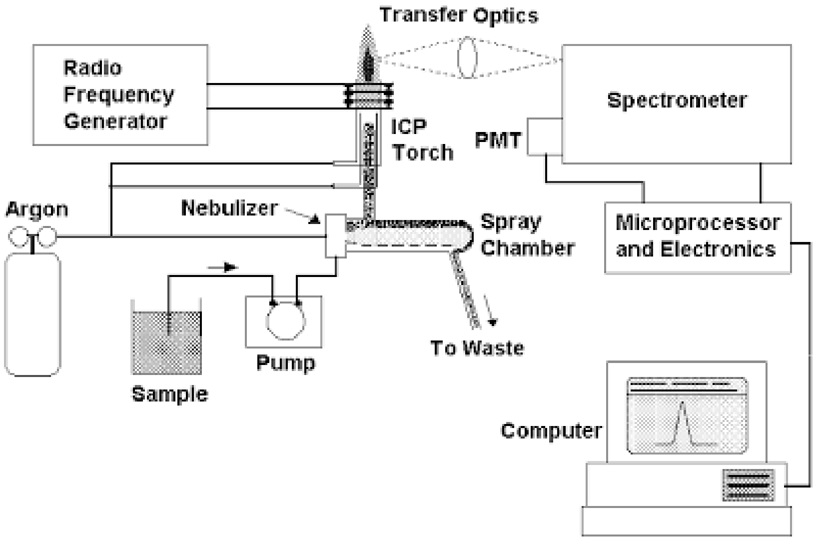
An Analysis of ICP-OES

Many water quality problems can't be directly observed, and often have similar symptoms - so how do we make proper changes? The answer will always be water testing. For the everyday parameters, home titration tests are still our most valuable method. However, knowing your system to an intimate degree requires an even closer look. Decoding the mystery of aquarium chemistry has become much easier with the availability of affordable trace element testing done specifically for the aquarium hobby.

ICP, an abbreviation for Inductively Coupled Plasma, is one method looking at elements that can't be measured with titration kits or elements present only in trace amounts. There are a few types of ICP methods, but the one used by all commercially available aquarium water testing services is called ICP-OES, or Optical Emission Spectroscopy. It is a natural fit for seawater analysis for the following reasons:

- Simultaneous analysis of multiple elements, eliminating the need for large samples or repeated testing
- Easy to read output
- Less chemical or ionization interference, allowing for analysis of high-matrix samples (samples that contain many elements)
- High sensitivity - can read trace concentrations to 10 ppb or lower for some elements
- Large number of measurable elements - elements that are difficult to analyze in other methods such as Zr, Ta, rare earth, P and B can be easily analyzed with ICP-OES

The sample of water you send in to an analysis company is usually diluted before it is sent into the ICP machine. When introduced into the ICP system, it is nebulized (sprayed into a very fine mist), mixed with argon gas and then superheated up to a toasty 10,000 Kelvin (for reference, this is almost double the temperature of the surface of the sun.) This separates all of the component atoms into highly excited states. It takes an extreme amount of energy to keep these atoms in excitation, so they quickly settle back to their ground states. During this settling process, each element emits photons in unique wavelengths that are observed by a spectrophotometer. This data is then compiled and analyzed by a spectroscopist. The element type is determined based on the position of the photon rays, and the content of each element is determined based on the rays' intensity.



Sample nebulized -> Sample superheated and cooled to produce light waves -> Light waves are recorded and analyzed

Every ICP-OES setup will have a unique configuration that could influence the output. It is very difficult to standardize, but there are ways to reduce experimental and analytical error. To understand the results, it is best to keep in mind the factors that influence them. Once the results have been recorded by the spectrophotometer and compiled into raw data, it is up to a spectroscopist to intepret what he or she sees.

PRECISION VS. ACCURACY

At first glance, these terms appear to work interchangeably and describe the same goal. In this application they are related, but refer to two different interpretations of the results.

Precision refers to the variability of many measurements. A highly precise instrument will "cluster" most of the measurements around a certain value, while an imprecise instrument will show values scattered around the detection field.

Accuracy is how close a measurement is to the true value. This can be especially tricky in this instance since the true value is unknown, and what we are trying to determine.

In the end we need both accuracy and precision. You want to consistently (this show reproducibility) be close to the true value with each measurement recorded. This can be achieved both mechanically, with high quality machines and software, and with training and experience when analyzing the output data.

Not accurate, not precise — Precise, not accurate — Accurate and precise

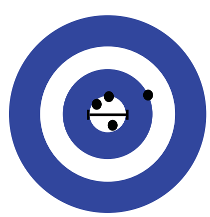
MARGIN OF ERROR & STANDARD DEVIATION

Margin of error is used widely in science and academia, but in spectroscopy it's not commonly used when referring to a spectrometer's capabilities. It is usually applied to specific tests and specific methods for a particular analyte or group of analytes. Error with this method is specific to each individual analysis - in relation to the "blank" or "rinse" solution. The analyte of interest should not theoretically be showing up in your blank solution. However, if it does, this can be used as a +/- error to normalize the output.

Standard deviation is used to quantify the amount of variation or dispersion of a set of data values. A low standard deviation indicates that the data points tend to be close to the expected value of the set, while a high standard deviation indicates that the data points are spread out over a wider range of values. This helps determine your "confidence level" and "precision" with respect to your data. There is a lot more to this story that isn't relevant to how to read the reports sent to end users, so I'll skip it.

Target shifted from interference

Margin of error is the difference between "normal" and "actual"



Statistically how close is each value relative to the rest of the dataset

SD helps "quantify" precision

CALIBRATION

ICP machinery is not calibrated in the traditional sense, like a refractometer may be. All of the measurements it takes are subjected to comparative samples. These may be “blanks,” which do not contain any of the elements being measured. Internal standards, samples that contain known amounts of specific elements, or elements in a matrix, are also used during testing to help determine any background noise which could get in the way when reading a result from an unknown.

The most common calibration technique options for ICP measurements are calibration curve and standard additions. In addition, the option of using internal standardization is available for the calibration curve technique and the ability of matrix matching may also be available. Many of these methods are used together to create the best conditions to measure with the most accuracy and precison.

LIMIT OF DETECTION

The limit of detection, or LOD, is simply the largest and smallest amount of analyte that can be determined with confidence. When it comes to detection limits, each manufacturer has their own detection limits for each specific technique and instrument model that is established from their in-house factory settings, but this is simply a company benchmark and not necessarily regulated. Real instrument detection limits and method detection limits are a bit of a moving target once they are installed in labs. They will change based upon the specific application.

DATA ANALYSIS

ICP-OES data analysis is a multi-step process. First, one must select the correct sample introduction method, as well as which plasma view and configuration to use. Then, method development must be carried out, taking into account possible interferences that need to be corrected for. Finally, evaluation of the method and its analytical results is conducted. In other words, every test and every type of test is handled in a unique way. In general, the commercially available saltwater testing companies have optimized and streamlined the process to provide their customers with quick and easy to read data. The best thing a consumer can do once they receive their report is educate themselves on how to interpret it.

Staying objective in a subjective world is almost impossible with any ICP system. If a measurement appears incorrect, it is up to the person analyzing the ICP output to identify any interferences, make judgement calls about wavelengths, retest, evaluate the calibration standard, etc. This is a labor intensive process that many analysis companies might not take on every single sample. However, some software is automating a lot of this process for unknown samples, like the ones we send in from our aquariums.

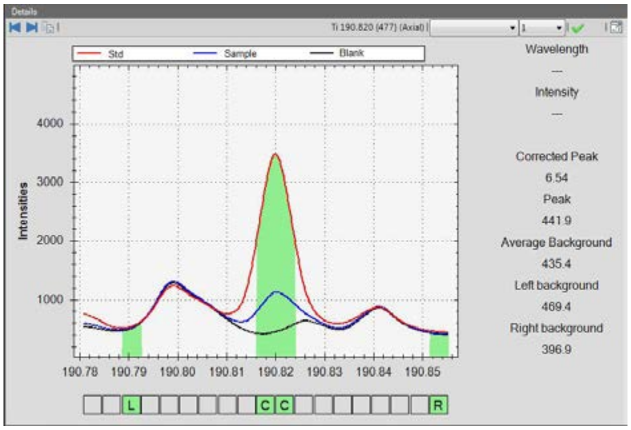


Fig. 2: Spectral interferences, as displayed in a subarray plot.

TEST RESULTS

To immerse ourselves in the world of ICP analysis, we sent in samples to four different commercially available water testing services to evaluate the consistency and reliability of the results within each company and between all being evaluated. For our experiment, one liter of saltwater was prepared using Fritz RPM salt (high alkalinity mix) and samples from the same batch were sent to each company for testing twice, about a month apart. Each sample was prepared according the the instructions provided with each kit. We paid for each test, they were not provided to us for this experiment.

All of the final reports we recieved back from our experimental testing gave indications of and suggestions for adjusting any values that fell outside of their “acceptable” range. This information may or may not be useful as each company has it’s own values and ranges for each element in natural seawater. They may also have an interest in selling their own supplements to help “correct” the results you receive. One difference between all of the available services is the elements they test and report overlap, but are not identical. For example, if you are interested in testing for Bismuth, the only company that provides a result for this element is ATI.

An important point to remember is elements are measured in total concentrations; this method does not discern the source of an element (inorganic/organic, molecular, ionic, etc). Iodine can have all four of the previously mentioned formed: ionic iodine (iodide, or I^-), molecular iodine (I_2), iodate (IO^-_3), and other organoiodine compounds. Looking at the results we received will not tell us exactly what kind of iodine is present, only that if we took the concentrations of every type of iodine atom present in the sample, they added up to the reported result. This can be frustrating for some elements, like iodine or copper, since in one form they are totally harmless, and in another they can be quite toxic.

When a measurement may not make sense, apply context: does a high reading of an element indicate the presence of a foreign object breaking down in the tank? Is it time to change the cartridges on the RO/DI system used for source water? Am I measuring the additive correctly for my tank? Has the salt been mixed to the correct salinity? Could the result have been misread by the company?

DISCUSSION

Overall, all of our results seem generally consistent, and accurate. It proved difficult to really “evaluate” each result individually, due to the sheer number of unknowns and variables that exist in the process. Errors that could have affected the results not related to the ICP process: sample was not exactly at 35 ppt, contamination in container or on tools I used to mix the salt water, salt blend might not have been uniform, source water may contain some dissolved solids.

Table 1: Triton indicated low lithium, high manganese, and high barium. ATI showed low Fluorine, and high manganese. ICP-Analysis.com showed only low iodine. Marinlab did not receive the sample sent, due to incorrect mailing address included in the package. Source RO/DI water was analyzed by ATI and showed no trace elements present.

Table 2: Triton indicated low lithium, high zinc, high manganese, and high barium. ATI showed low Fluorine, and high manganese. ICP-A showed low magnesium, low sodium, and low sulfur. Marinlab indicated high barium, low lithium, high manganese, and high boron. Source RO/DI water was analyzed by Marinlab and reported only high amounts of silicon but this did not contribute to a high level of overall silicon in the mixed saltwater.

Table 3: Since the only values available that are fixed are the theoretical values of each element of the salt mix, it is challenging to compare our results to anything else with total confidence. However, theoretical values can be used as a benchmark to increase confidence in other results. Similar results from multiple tests within and across companies also increase confidence. Results have been color coded according to confidence level. Green shows a high confidence level, red a low confidence level, and no color indicates neither confident or unconfident about the result.

Element	Triton	Triton Setpoint	ATI	ATI Setpoint	ICP-A	ICP-A Setpoint	Marinlab	Marinlab Setpoint	Fritz QC (34678.8)	RO (ATI)
Salinity			34.57	35 ppt					35 ppt	
Alkalinity			10.63	7.5 dKH					10.36 dKH	
						(Fiji)				
Ag			0.00	0.1 µg/L	4.6	1 µg/L				0
Al	2.92	2 µg/L	0.84	0.1 µg/L	47	50 µg/L		0-10 µg/L		0
As	0.00	0 µg/L	0.00	1.48 µg/L	1	10 µg/L		0-3 µg/L		0
B	4.58	4.5 mg/L	6	4.35 mg/L	6.12	4.57 mg/L		4.05-5 mg/L		0
Ba	67.00	10 µg/L	50.96	9.88 µg/L	90	0 µg/L		0-40 µg/L		0
Be	0.00	0 µg/L	0.00	0.1 µg/L	0	0 µg/L		0 µg/L		0
Bi			0.00	0.1 µg/L						0
Br	45.00	62 mg/L	49.72	66.18 mg/L	63.25	51.35 mg/L		55-74 mg/L		0
Ca	429	440 mg/L	465.8	415.8 mg/L	439.05	397.67 mg/L		380-460 mg/L	410 mg/L	0
Cd	0.00	0 µg/L	0.00	0.2 µg/L	1	0 µg/L		0-0.2 µg/L		0
Ce					0	1 µg/L				
Cl			19943	19557 mg/L	18456.67	18427.15 mg/L				0
Co	0.00	0 µg/L	0.00	0.1 µg/L	2	10 µg/L		0-0.6 µg/L		0
Cr	0.00	0 µg/L	0.00	0.49 µg/L	0	20 µg/L		0-0.4 µg/L		0
Cu	0.00	0 µg/L	0.00	0.49 µg/L	0	0 µg/L		0-1.2 µg/L		0
F			0.25	1.28 mg/L						0
Fe	0.00	0 µg/L	0.00	0.49 µg/L	1	1 µg/L		0-6 µg/L		0
Ga					15	10 µg/L				
Hg	0.00	0 µg/L	0.00	0 µg/L				0 µg/L		0
I	41.00	60 µg/L	44.32	64.2 µg/L	20	41 µg/L		55-70 µg/L		0
K	395	400 mg/L	457.6	403 mg/L	428.49	384.69 mg/L		360-420 µg/L		0
La	0.00	0 µg/L	0.00	0 µg/L	7	7 µg/L		0 µg/L		0
Li	110.0	200 µg/L	90.36	167.9 µg/L	55	180 µg/L		150-200 µg/L		0
Mg	1331	1370 mg/L	1419	1299 mg/L	1328.40	1239.34 mg/L		1188-1460 mg/L	1350 mg/L	0
Mn	117.00	2 µg/L	104.1	0.99 µg/L	30	0 µg/L		0-2.2 µg/L		0
Mo	3.46	12 µg/L	6.95	11.85 µg/L	2	15 µg/L		4.5-12 µg/L		0
Na	10074	10700 mg/L	10651	10865 mg/L	9943.54	10505.98 mg/L		9720-11880		0
Ni	0.00	5 µg/L	1.31	0.49 µg/L	1	10 µg/L		0-10 µg/L		0
NO3			0.61	2 mg/L						0
P	11	6 µg/L	13.78	14.82 µg/L	10	50 µg/L		0-6 µg/L		0
PO4	0.034	0.018 mg/L	0.04	0.04 mg/L				0-0.01 µg/L	0.00 mg/L	0
Pb	0.00	0 µg/L	0.00	0.1 µg/L	24	11 µg/L		0 µg/L		0
Rb					0	0 µg/L				
S	801.00	900 mg/L	801.5	908.7 mg/L	718.89	834.73 mg/L		810-990 mg/L		0
Sb	0.00	0 µg/L	0.00	0.1 µg/L	0	7 µg/L		0-0.5		0
Sc	0.00	0 µg/L						0 µg/L		
Se	0.00	0 µg/L	0.00	0.49 µg/L	26	0 µg/L		0-1.5 µg/L		0
Si	96.00	100 µg/L	66.14	98.77 µg/L	271	0 µg/L		20-2900 µg/L		0
Sn	0.00	0 µg/L	0.00	0.49 µg/L	0	10 µg/L		0-1 µg/L		0
Sr	5.74	8 mg/L	9.62	7.9 mg/L	8.61	7.47 mg/L		7.2-8.8 mg/L		0
Ti	0.00	0 µg/L	0.00	0.1 µg/L	0	0 µg/L				0
Tl			0.00	0.1 µg/L	0	0 µg/L		0-10 µg/L		0
U					48	21 µg/L				
V	0.00	1.2 µg/L	0.69	1.48 µg/L	2.4	0.5 µg/L		0-2.5 µg/L		0
W	0.00	0 µg/L	0.00	0 µg/L	8	7 µg/L		0 µg/L		0
Zn	0.00	4 µg/L	0.00	1.98 µg/L	0	2 µg/L		0-7 µg/L		0

Table 1: Round 1 of RPM saltwater results by company

Element	Triton	Triton Setpoint	ATI	ATI Setpoint	ICP-A	ICP-A Setpoint	Marinlab	Marinlab Setpoint	Fritz QC (34678.8)	RO (Marinlab)
Salinity			33.58	35 ppt			34		35 ppt	
Alkalinity			10.69	7.5 dKH			10.4		10.36 dKH	
Ag			0.00	0.1 µg/L	3.1	1 µg/L				
Al	6.4	2 µg/L	1.98	0.1 µg/L	34	50 µg/L	7.8	0-10 µg/L		0.1 µg/L
As	0	0 µg/L	0.00	1.48 µg/L	0	10 µg/L	0	0-3 µg/L		0 µg/L
B	5.41	4.5 mg/L	5.99	4.35 mg/L	5.72	4.57 mg/L	6.14	4.05-5 mg/L		0 µg/L
Ba	104	10 µg/L	83.15	9.88 µg/L	90	0 µg/L	88	0-40 µg/L		0.3 µg/L
Be	0	0 µg/L	0.00	0.1 µg/L	0	0 µg/L	0	0 µg/L		0 µg/L
Bi			0.00	0.1 µg/L						
Br	51	62 mg/L	48	66.18 mg/L	53.81	51.35 mg/L	52.1	55-74 mg/L		0 µg/L
Ca	459	440 mg/L	463.9	415.8 mg/L	379.08	397.67 mg/L	454	380-460 mg/L	410 mg/L	23 µg/L
Cd	0	0 µg/L	0.00	0.2 µg/L	1	0 µg/L	0	0-0.2 µg/L		0 µg/L
Ce					1	1 µg/L				
Cl			19398	19557 mg/L	17359.34	18427.15 mg/L				
Co	0	0 µg/L	0.00	0.1 µg/L	11	10 µg/L	0	0-0.6 µg/L		0 µg/L
Cr	0	0 µg/L	0.00	0.49 µg/L	0	20 µg/L	0	0-0.4 µg/L		0 µg/L
Cu	0	0 µg/L	0.00	0.49 µg/L	0	0 µg/L	0	0-1.2 µg/L		0 µg/L
F			0.22	1.28 mg/L						
Fe	0	0 µg/L	0.00	0.49 µg/L	0	1 µg/L	0	0-6 µg/L		0 µg/L
Ga					30	10 µg/L				
Hg	0	0 µg/L	0.00	0 µg/L			0	0 µg/L		0 µg/L
I	53	60 µg/L	45	64.2 µg/L	50	41 µg/L	79.1	55-70 µg/L		
K	425	400 mg/L	439.1	403 mg/L	352.77	384.69 mg/L	427	360-420 µg/L		31 µg/L
La	0	0 µg/L	0.00	0 µg/L	7	7 µg/L	0	0 µg/L		0 µg/L
Li	96	200 µg/L	65.55	167.9 µg/L	45	180 µg/L	59.7	150-200 µg/L		0 µg/L
Mg	1440	1370 mg/L	1382	1299 mg/L	1184.54	1239.34 mg/L	1364	1188-1460 mg/L	1350 mg/L	0.26 mg/L
Mn	152	2 µg/L	129.9	0.99 µg/L	30	0 µg/L	167	0-2.2 µg/L		0.2 µg/L
Mo	5.05	12 µg/L	4.12	11.85 µg/L	3	15 µg/L	5.2	4.5-12 µg/L		0 µg/L
Na	10419	10700 mg/L	10332	10865 mg/L	8858.11	10505.98 mg/L	10502	9720-11880		1.61 mg/L
Ni	2.16	5 µg/L	0.81	0.49 µg/L	7	10 µg/L	2.1	0-10 µg/L		0 µg/L
NO3			0.31	2 mg/L						
P	5.77	6 µg/L	4.89	14.82 µg/L	0	50 µg/L	12.9	0-6 µg/L		0 µg/L
PO4	0.018	0.018 mg/L	0.01	0.04 mg/L			39.5	0-0.01 µg/L	0.00 mg/L	0 µg/L
Pb	0	0 µg/L	0.00	0.1 µg/L	0	11 µg/L	0	0 µg/L		0 µg/L
Rb					0	0 µg/L				
S	785	900 mg/L	775.4	908.7 mg/L	668.53	834.73 mg/L	849	810-990 mg/L		0.16 mg/L
Sb	0	0 µg/L	0.00	0.1 µg/L	0.014	7 µg/L	0	0-0.5		0 µg/L
Sc	0	0 µg/L					0	0 µg/L		0 µg/L
Se	0	0 µg/L	0.00	0.49 µg/L	0	0 µg/L	0	0-1.5 µg/L		0 µg/L
Si	182	100 µg/L	87.88	98.77 µg/L	189	0 µg/L	82.7	20-2900 µg/L		12.8 µg/L
Sn	0	0 µg/L	0.00	0.49 µg/L	23	10 µg/L	0	0-1 µg/L		0 µg/L
Sr	10	8 mg/L	9.71	7.9 mg/L	8.31	7.47 mg/L	9.36	7.2-8.8 mg/L		0.002 mg/L
Ti	0	0 µg/L	0.00	0.1 µg/L	0	0 µg/L	0	0-10 µg/L		0 µg/L
Tl			0.00	0.1 µg/L	0	0 µg/L				
U					36	21 µg/L				
V	0	1.2 µg/L	0.00	1.48 µg/L	1.9	0.5 µg/L	0	0-2.5 µg/L		0 µg/L
W	0	0 µg/L	0.00	0 µg/L	6	7 µg/L	0	0 µg/L		0 µg/L
Zn	87	4 µg/L	1.13	1.98 µg/L	0	2 µg/L	2.4	0-7 µg/L		0.3 µg/L

Table 2: Round 2 of RPM saltwater results by company

Element	RPM Theoretical Value	Triton Test 1	Triton Test 2	Triton Setpoint		ATI Test 1	ATI Test 2	ATI Setpoint		ICP-A Test 1	ICP-A Test 2	ICP-A Setpoint
Salinity	35 ppt					34.57	33.58	35 ppt				
Alkalinity	10 dKH					10.63	10.69	7.5 dKH				
Ag	0					0.00	0.00	0.1 µg/L		4.6	3.1	1 µg/L
Al	0	2.92	6.4	2 µg/L		0.84	1.98	0.1 µg/L		47	34	50 µg/L
As	0	0.00	0.00	0 µg/L		0.00	0.00	1.48 µg/L		1	0.00	10 µg/L
B	5 mg/L	4.58	5.41	4.5 mg/L		6	5.99	4.35 mg/L		6.12	5.72	4.57 mg/L
Ba	0	67.00	104	10 µg/L		50.96	83.15	9.88 µg/L		90	90	0 µg/L
Be	0	0.00	0.00	0 µg/L		0.00	0.00	0.1 µg/L		0.00	0.00	0 µg/L
Bi	0					0.00	0.00	0.1 µg/L				
Br	0	45.00	51	62 mg/L		49.72	48	66.18 mg/L		63.25	53.81	51.35 mg/L
Ca	420 mg/L	429	459	440 mg/L		465.8	463.9	415.8 mg/L		439.05	379.08	397.67 mg/L
Cd	0	0.00	0.00	0 µg/L		0.00	0.00	0.2 µg/L		1	1	0 µg/L
Ce	0									0.00	1	1 µg/L
Cl	0					19943	19398	19557 mg/L		18456.67	17359.34	18427.15 mg/L
Co	0	0.00	0.00	0 µg/L		0.00	0.00	0.1 µg/L		2	11	10 µg/L
Cr	0	0.00	0.00	0 µg/L		0.00	0.00	0.49 µg/L		0.00	0.00	20 µg/L
Cu	0	0.00	0.00	0 µg/L		0.00	0.00	0.49 µg/L		0.00	0.00	0 µg/L
F	0					0.25	0.22	1.28 mg/L				
Fe	0	0.00	0.00	0 µg/L		0.00	0.00	0.49 µg/L		1	0.00	1 µg/L
Ga	0									15	30	10 µg/L
Hg	0	0.00	0.00	0 µg/L		0.00	0.00	0 µg/L				
I	44 µg/L	41.00	53	60 µg/L		44.32	45	64.2 µg/L		20	50	41 µg/L
K	384 mg/L	395	425	400 mg/L		457.6	439.1	403 mg/L		428.49	352.77	384.69 mg/L
La	0	0.00	0.00	0 µg/L		0.00	0.00	0 µg/L		7	7	7 µg/L
Li	0	110.0	96	200 µg/L		90.36	65.55	167.9 µg/L		55	45	180 µg/L
Mg	1306 mg/L	1331	1440	1370 mg/L		1419	1382	1299 mg/L		1328.40	1184.54	1239.34 mg/L
Mn	0	117.00	152	2 µg/L		104.1	129.9	0.99 µg/L		30	30	0 µg/L
Mo	23 µg/L	3.46	5.05	12 µg/L		6.95	4.12	11.85 µg/L		2	3	15 µg/L
Na	9326 mg/L	10074	10419	10700 mg/L		10651	10332	10865 mg/L		9943.54	8858.11	10505.98 mg/L
Ni	0	0.00	2.16	5 µg/L		1.31	0.81	0.49 µg/L		1	7	10 µg/L
NO3	0					0.61	0.31	2 mg/L				
P	0	11	5.77	6 µg/L		13.78	4.89	14.82 µg/L		10	0.00	50 µg/L
PO4	0	0.034	0.018	0.018 mg/L		0.04	0.01	0.04 mg/L				
Pb	0	0.00	0.00	0 µg/L		0.00	0.00	0.1 µg/L		24	0.00	11 µg/L
Rb	0									0.00	0.00	0 µg/L
S	750 mg/L	801.00	785	900 mg/L		801.5	775.4	908.7 mg/L		718.89	668.53	834.73 mg/L
Sb	0	0.00	0.00	0 µg/L		0.00	0.00	0.1 µg/L		0.00	0.014	7 µg/L
Sc	0	0.00	0.00	0 µg/L								
Se	0	0.00	0.00	0 µg/L		0.00	0.00	0.49 µg/L		26	0.00	0 µg/L
Si	0	96.00	182	100 µg/L		66.14	87.88	98.77 µg/L		271	189	0 µg/L
Sn	0	0.00	0.00	0 µg/L		0.00	0.00	0.49 µg/L		0.00	23	10 µg/L
Sr	8.6 mg/L	5.74	10	8 mg/L		9.62	9.71	7.9 mg/L		8.61	8.31	7.47 mg/L
Ti	0	0.00	0.00	0 µg/L		0.00	0.00	0.1 µg/L		0.00	0.00	0 µg/L
Tl	0					0.00	0.00	0.1 µg/L		0.00	0.00	0 µg/L
U	0									48	36	21 µg/L
V	0	0.00	0.00	1.2 µg/L		0.69	0.00	1.48 µg/L		2.4	1.9	0.5 µg/L
W	0	0.00	0.00	0 µg/L		0.00	0.00	0 µg/L		8	6	7 µg/L
Zn	0	0.00	87	4 µg/L		0.00	1.13	1.98 µg/L		0.00	0.00	2 µg/L

Table 3: RPM saltwater results comparison

SERVICE EVALUATIONS

Triton: The good: Triton had fast service (despite sending samples all the way to Germany!), with a report a few business days after the received the sample. In my case it took about 10 days. The results are easy to read, and offer helpful suggestions to find the source of a high or low result. Triton has been in business long enough to become the reliable industry standard.

The bad: The website was not the most user friendly, I had a lot of trouble setting up an account due to browser incompatibilities. The report does not give values on the ranges that display the results - only colors. This limits the sense of scale of how "off" a result may be.

Overall: A- The results were overall acceptable and consistent with other companies in the experiment. They do not provide results from more obscure elements like others do (Ag, Ce, Ga, U, etc) but they have probably determined these are not necessary or cost/time effective. I would have preferred a salinity and alkalinity measurement, as that can set the tone for the rest of the results. $49

ATI: The good: The results were returned quickly, between 1 and 2 weeks from shipping. ATI also offers free testing of RO water with every kit. A pre-paid shipping label is also included in the kit.

The bad: The website was not the most user friendly, my notifications went to my e-mail spam folder so I didn't know my results were ready

Overall: A The results were consistent and comparable with Triton and Marinlab. Everything about the kit was easy to follow and the inclusion of the shipping label was a definite plus eliminating the need to go to the post office. $45

ICP-Analysis.com: The good: The website is robust and displays results in an easy to understand manner. It also allows the user to change the NSW reference point to match their preferred environment. The test kit was also the least expensive of the four companies in the experiment.

The bad: All results were presented in ppm, which can be confusing if trying to compare to other measurements in mg/L or ug/L. My first sample got lost in the mail, marked delivered by USPS but not received by the company (they indicated this happens a few times a week.) My subsequent samples I sent with additional postage requiring signature upon receipt, at a higher cost to me.

Overall: C- When compared to other companies, ICP-A results frequently did not follow the trends seen in other tests. Some of the setpoints were significantly different compared to other companies as well. I believe ICP-Analysis is a relatively new company, so perhaps these things will be adjusted over time. $30

Marinlab: The good: the website is robust and displays results in an easy to understand manner. The results are presented in a manner similar to Triton, on a color coded scale, making quick reference easy. Marinlab also offers an acceptable range when evaluating results rather than a singular setpoint. They also offer RO water testing for an additonal fee.

The bad: Because the Marinlab testing facility is in Europe, test kits are first sent to a US address and forwarded from there. That address changed in the last couple of years, but some kits still have the old mailing address inside. There is a warning on the website, but I missed it the first time and my sample was not delivered to Marinlab, or back to me. My second sample did arrive and was tested, but it took a month to get results back. Due to that I was unable to send another sample in time to receive results for this comparison.

Overall: B+ I found the results I was able to get back very comparable and consistent with both Triton and ATI. The shipping issue was mostly an accident, and should resolve itself as new kits are produced with the correct mailing address inside. The company did respond to my questions through their contact form, and will honor the code purchased for the lost sample for a future test. $30-40

SUMMARY AND CONCLUSION

Testing with ICP-OES is far from being the gospel many think it is. It can a very valuable tool in a complete aquarium tool kit, when utilized correctly. Some hard-to-solve problems can be explained and eventual issues can be avoided with ICP-OES water testing. It does not, however, replace good husbandry and regular testing with available quicker test methods.

Always use available titration kits when possible. They are far more cost effective, reliable, and replicable than one ICP test.

Beware of "supplement systems" ICP companies offer to solve problems they find with your samples. These may not be harmful, but before investing in additional supplements, determine the source of your issue before attempting to fix it.

Get a second, and maybe third, opinion - one test is not enough. If it is in your budget, test regularly, and try out multiple companies. The more results you have over time, the clearer the picture will be. Also don't be afraid to ask the testing company questions of you aren't sure about an outlier result. Feedback can help them identify problem areas and adjust their process for the future and other customers.

Be satisfied with a "close enough" result. There will never be a test method to give you an exact true concentration of any element present in a water sample. Values within an acceptable range should not be stressed over, this is a normal part of the process. If something concerns you, read more about the potential issue online, ask others in forums, and contact the company for more information. Natural sea water changes throughout the world, no two places will look alike in terms of components.

Evaluate the overall health of your tank visually. Are your fish and corals healthy and growing? Has anything changed in your routine the last few weeks or months? Most of the time, your animals will indicate if there is a serious problem.

Choose an ICP testing service that is right for you. They all have strengths and weaknesses, but all offer a bit deeper look into your aquarium.

UNDERSTANDING THE ELEMENTS

Silver (Ag): Silver has been shown to have antibacterial, antiviral, antifungal, and algaecidal properties, and may pose the biggest threat in natural environments by upsetting the food chain. Silver has also been observed to affect the gills in fish and invertebrates.
Major Sources: Impurity in aquarium additives/salts, jewelry, naturally occuring in substrates
Concern: **Moderate.** Seawater contains approximately 2-100 ppt, much higher than should be attainable in an aquarium, although some studies show acute toxicity above 0.01 ug/L Read More
Removal: Water changes, discontinuation of additives that contain Ag

Aluminum (Al): Aluminum is an ion that does not get much attention, and has no clear biological use in aquaria. It can, however, have an impact on aquarium organisms if elevated sufficiently over natural levels. Seems to have more of an effect on soft corals than stony.
Major Sources: Aluminum-based phosphate removers, foods
Concern: **Low.** Dangerous to some aquaria in levels above 500ppm. Read More
Removal: Water changes, discontinuation of aluminum-based phosphate removers

Arsenic (As): Toxic and other effects of arsenicals to aquatic life are significantly modified by numerous biological and abiotic factors, water temperature, pH, Eh, organic content, phosphate concentration, suspended solids, and presence of other substances and toxicants, as well as arsenic speciation, and duration of exposure.
Major Sources: impurity in aquarium additives/salts
Concern: **Low.** The general accepted max concentration is 0.01 mg/L, much more than should be atainable in an aquarium. Read More
Removal: Water changes, discontinuation of additives that contain As

Boron (B): The most commonly known property of Boron, in the forms of boric acid and borate, is its ability to buffer seawater against pH changes. At boron levels above that present in natural seawater, as is supplied in some artificial salt mixes and as may develop from overuse of boron supplements, boron begins to exert undesirable toxicity on a number of organisms.
Major Sources: Foods, $CaCO_3/CO_2$ reactor media that contains substantial boron, calcium and alkalinity supplements with incidental or intentionally added boron
Concern: **Low.** Values above 10 ppm should be avoided. Read More
Removal: Water changes, macroalgae harvesting

Barium (Ba): The value of barium in NSW is deceivingly low despite it being quite prolific in the ocean. Barium is quite common in marine sediments, soft animal tissues, and coral skeletons (and subsequently aragonite-based substrates.)
Major Sources: Impurity in salt mixes and potentially other additives, like GFO
Concern: **None.** Not particularly toxic even at extreme levels Read More
Removal: Not necessary; no reliable known method besides water changes with low-barium salt mix

Beryllium (Be): There is no scientific data on the toxicity of Beryllium in reef ecosystems, but it is highly toxic to humans.
Major Sources: None
Concern: **Low.** Very few sources for significant introduction into an aquarium. Read More
Removal: Discontinuation of additives containing Beryllium, water changes

Bismuth (Bi): There is no scientific data on the toxicity of Bismuth in reef ecosystems, but it is highly toxic to humans in the form of Bismuth Nitrate.
Major Sources: None
Concern: **Low.** Very few sources for significant introduction into an aquarium. Read More
Removal: Water changes

Bromine (Br): Stony corals use bromine in two different ways, first for chromoprotein synthesis and secondly for skeleton construction, as sodium bromide. Furthermore zooxantellae need small amount of bromine for the synthesis of photosynthetic enzymes. The biggest issue will be those using ozone, which easily oxidizes bromide to a bromine bleach.
Major Sources: Impurity or intentional in aquarium additives/salts
Concern: **Moderate.** Toxicity is well documented, but removal is easily achieved. Safe at concentrations similar to NSW Read More
Removal: Using GAC will remove toxic compounds, water changes, discontinuation of additives containing bromine

Cadmium (Cd): Cadmium is a non-essential metal with no biological function in aquatic animals. Toxic effects are thought to result from the free ionic form of cadmium, which causes acute and chronic toxicity in aquatic organisms primarily by disrupting calcium homeostasis and causing oxidative damage.
Major Sources: Impurity in aquarium additives/salts
Concern: **None.** The most sensitive organism studied showed effects of toxicity at 29 ug/l, or 0.029 ppm. This level will never be reached in a reef aquarium. Read More
Removal: Not necessary; no reliable known method besides water changes with low-cadmium salt mix

Cesium (Ce): A naturally-occurring element found in rocks, soil and dust at low concentrations. It is present in the environment only in the stable form of 133 Cesium (the radioactive isotopes 134 Cesium and 137 Cesium are usually not measured or reported). There is no scientific data on the toxicity of Cesium in reef ecosystems.
Major Sources: None
Concern: **None.** Read More
Removal: Not necessary; water changes

Cobalt (Co): Below 0.1 ug/L, cobalt is thought to increase coral coloration. A moderate cobalt concentration (0.2 µg/L), and without interaction with acidification, adversely affects the growth of some coral species and that an increase in cobalt concentration to 1.06 µg/L leads not only to coral growth decrease, but also to an inhibition of their photosynthesis process
Major Sources: Cobalt additives
Concern: **Low.** Unless adding cobalt directly, concentration shouldn't reach a dangerous level in an aquarium. Read More
Removal: Water changes, discontinuation of cobalt-containing additives

Chromium (Cr): According to some trace element additives, it boosts green coloration in corals
Major Sources: Trace element additives, impurity in aquarium additives/salts
Concern: **None.** The most sensitive organism studied showed effects of toxicity at 5 ppm. This level will never be reached in a reef aquarium without extreme overdosing of trace element supplements. Read More
Removal: Not necessary; no reliable known method besides water changes with low-chromium salt mix

Copper (Cu): Organic copper is necessary for some cellular functions. Inorganic copper, the form found in most medications and as impurities, is toxic to invertebrates and corals in low concentrations.
Major Sources: Copper-based medications, foods, trace element additives, impurity in aquarium additives/salts, tap water
Concern: **Moderate to High.** Much of the inorganic copper will be converted to harmless organic copper over time, but will initially be dangerous for inverts. Carefully dose copper meds according to instructions, not to exceed 0.6 ppm ionic copper (chelated copper is used at much higher concentrations. Read More
Removal: Copper-adsorbing resins, activated carbon (organic only), polyfilters (organic only), water changes with low-copper salt mix

Flourine (F): Fluorine is useful for coral calcification process. However fluorine is capable of irreversibly inhibiting photosynthetic enzymes causing zooxanthellae loss in coral tissues.
Major Sources: Halogen supplements containing fluorine (as flouride)
Concern: **Low.** Fluorine in concentrations close to NSW should be sufficient in most situations. Read More
Removal: Water changes, discontinuation of additives containing Fluorine

Iron (Fe): Iron encourages growth of macroalgae, which in turn increases nutrient export and outcompeting microalgaes. Iron is also necessary for respiration in animals with iron-based blood.
Major Sources: Iron supplements, impurity from in aquarium additives/salts
Concern: **None.** Not particularly toxic even at extreme levels. Read More
Removal: Not necessary; macroalgae harvesting

Gallium (Ga): There is no scientific data on the toxicity of Gallium in reef ecosystems. It does not show toxicity to humans unless purposefully ingested in large amounts.
Major Sources: Environmental impurities, impurity from in aquarium additives/salts
Concern: **Low.** If no signs of distress, concentrations near NSW should be safe. Read More
Removal: Water changes

Mercury (Hg): Mercury is naturally occurring element in the Earth's crust that is released into the environment with natural events such as volcanic activity. Mercury commonly occurs in three forms: elemental, inorganic and organic, and is passed up the food chain through biomagnification.
Major Sources: Mercury-based thermometers, foods containing wild fish meal
Concern: **Low.** If no signs of distress, concentrations near NSW should be safe. Read More
Removal: Water changes

Iodine (I): Lugols' solution, for example, contains a mixture of I_2 and I^-. It is the I_2 form in particular that is the basis for the widespread belief that iodine is "toxic." The I_2 form, and that form in combination with other forms, it is a potent antibacterial agent that has long been used for disinfection. The naturally occurring inorganic forms (iodide and iodate) have little in the way of antimicrobial activity and show little toxicity.
Major Sources: foods containing algae, impurities in additives/salt, iodine supplements
Concern: **Low.** 0.06 ppm is normal, but keep in mind this includes all species of iodine (organic and inorganic) Read More
Removal: Water changes, discontinuation of Iodine supplements

Potassium (K): Potassium, unlike elements such as calcium, is not strictly limiting for coral life. Indeed a lack of potassium is not dangerous until it reaches very low values. Calcium under 350 mg/l can be fatal to more sensitive corals, but potassium values under 200 mg/l can be tolerated by most coral species. Furthermore the symptoms of the lack of potassium are extremely diverse and nonspecific.
Major Sources: normal ingredient in many salts and aquarium additives and foods
Concern: **Low.** Sticking to around 400 ppm is sufficient. Higher concentrations achieved over time are generally not problematic, however a single large dose can cause tissue necrosis in corals. Read More
Removal: Water changes, discontinuation of potassium supplements

Lanthanum (La): Sometimes used as a phosphate remover, Lanthanum can cause a lot of distress in corals and fish if allowed to enter into a display tank. If used for this purpose a lot of care must be taken to remove it quickly. Lanthanum compounds can also cause alkalinity to drop rapidly.
Concern: **Moderate.** Unless dosing for phosphate control, lanthanum concentrations should not generally be measurable. Read More
Removal: Water changes, fine micron filters, skimming, discontinuation of lanthanum supplements

Lithium (Li): Little study has been done on lithium toxicity in aquariums, but generally is not regarded as a dangerous element in concentrations attainable in reef aquaria above levels found in natural seawater .
Major Sources: Impurity in aquarium additives/salts
Concern: **Low.** Read More
Removal: No reliable known method besides water changes with low-lithium salt mix

Manganese (Mn): Common as a fertilizer for plants in freshwater tanks, and algaes in saltwater tanks. Known to be scavenged by phytoplankton, possibly accounting for low levels in NSW.
Major Sources: Aquarium additives, foods, impurity in aquarium additives/salts
Concern: **Low.** Manganese is commonly paired with iron for supplementation, but the levels occurring with regular salt mixes are generally sufficient for most tanks. Read More
Removal: Not necessary; water changes or discontinuation of additives containing Mn

Molybdenum (Mo): Molybdenum is important for the biological processes of bacteria, and may be of some benefit to corals as well. High levels of molybdenum are known to encourage blooms of slime algae or cyanobacteria.
Major Sources: Aquarium additives, foods, impurity in aquarium additives/salts
Concern: **Low.** Molybdenum is commonly paired with strontium for supplementation, but the levels occurring with regular salt mixes are generally sufficient for most tanks. 0.12 mg/L is the upper toxicity limit for Molybdenum.
Removal: Water changes or discontinuation of additives containing Mo

Nickel (Ni): Nickel is a ubiquitous trace metal and occurs in soil, water, air, and in the biosphere.
Major Sources: Exposed metal in the aquarium, aquarium additives, foods, impurity in aquarium additives/salts
Concern: **Low.** Little toxicity was found above 0.02 ppm Read More
Removal: Water changes, some phosphate removers, activated carbon

Phosphorus (P): Phosphorus is a limiting nutrient in saltwater systems and an excess can result in eutrophication, which promotes excess growth of algae and saltwater plants. As plants and algae grow and consequently die and decay, this decomposition consumes available oxygen and can lead to hypoxic (low oxygen) conditions.
Major Sources: Foods, aquarium additives, source water, impurity in aquarium additives/salts
Concern: **Moderate.** If phosphorus is present in concentrations greater than 30 ppb, the precipitation of calcium carbonate may be inhibited for certain species of coral. Read More
Removal: Phosphate removers, water changes

Lead (Pb): Lead is a metal with no known beneficial role in biological systems. Not much scientific data exists about the specific impact of lead on a reef aquarium, but due to its known toxicity in humans and other animals it should be avoided.
Major Sources: Foods, unfiltered source water/lead pipes,
Concern: **Moderate.** While generally rare, avoid any measurable concentration. Read More
Removal: Water changes, heavy metal adsorbers

Rubidium (Rb): Very similar to potassium, The two elements are found together in minerals and soils. Rubidium has no known biological role but has a slight slimulatory effect on metabolis (most likely in potassium-poor environments and acting in place of potassium.)
Major Sources: Impurity in additives
Concern: **None.** Measurable concentrations should be rare. Read More
Removal: Water changes, algae export

Sulfur (S): There are many forms of sulfur in an aquarium, most beneficial, and some dangerous. Under anoxic conditions some bacteria can use sulfate to metabolize organic material, producing hydrogen sulfide (H_2S) as a byproduct.
Major Sources: Natural part of seawater
Concern: **Low.** Sulfates are not harmful, hydrogen sulfides can be, but the toxic concentration is variable depending on the species Read More
Removal: Not necessary. When a "sulfur smell" is present - water changes, increased circulation/removal of anoxic conditions

Antimony (Sb): The source of antimony in NSW is attributed mostly to atmospheric pollution.
Major Sources: None
Concern: **Low.** Measurable concentrations should be rare. Read More
Removal: Water changes

Scandium (Sc): Scandium is distributed widely, occurring in trace quantities in over 800 minerals. It has no known use in biology.
Major Sources: None
Concern: **Low.** Measurable concentrations should be rare. Read More
Removal: Water changes

Selenium (Se): Selenium is an essential micronutrient due to its requirement for biosynthesis and function of the amino acid selenocysteine (Sec). It is found throughout the ocean in various stages of a selenium cycle. It can reach toxic levels through bioaccumulation through the food chain.
Major Sources: Foods
Concern: **Low.** Measurable concentrations should be rare. Read More
Removal: Water changes

Silicon (Si): Silicon dioxide is a dietary requirement for various organisms. Diatoms and sea sponges apply silicon for skeleton strengthening. In the surface layers of oceans silicon concentrations are 30 ppb, whereas deeper water layers may contain 2 ppm silicon.
Major Sources: Aquarium additives and salts
Concern: **Moderate.** Higher levels of silicon can cause diatom blooms Read More
Removal: Water changes

Tin (Sn): Organic tins are known to disturb growth, reproduction, enzymatic systems and feeding patterns of aquatic organisms.
Major Sources: Leaching from metals in or around the system
Concern: **None.** Tin has an average concentration in our systems of over 200,000 times greater than in natural sea water. Read More
Removal: Water changes, removal of exposed metals

Strontium (Sr): The strontium ion is very similar to calcium and magnesium ions and has been found to be incorporated into coral skeletons to some degree. There is debate over whether supplementation is necessary above levels encountered from incidental addition.
Major Sources: Aquarium additives, kalkwasser, impurity in aquarium additives/salts
Concern: **Low.** High concentration can cause calcium precipitation. Read More
Removal: Water changes

Titanium (Ti): Titanium dioxide suppresses the immune response in fish. However, high grade titanium metal does not corrode to a measurable degree when exposed to saltwater.
Major Sources: Sunblock containing titanium dioxide, titanium heaters/chillers/probes
Concern: **None.** Measurable concentrations should be rare, and if so, shouldn't cause any alarm. Read More
Removal: Water changes

Thallium (Tl): Thallium displays toxicity similar to copper in symptoms and concentrations.
Major Sources: Natural mud/clay substrates
Concern: **Low.** Measurable concentrations should be rare. Read More
Removal: Water changes, algae export

Uranium (U): There is no scientific data on the toxicity of Uranium in reef ecosystems.
Major Sources: Environmental
Concern: **Low.** Measurable concentrations should be rare.
Removal: Water changes

Vanadium (V): Necessary for growth in sponges and other ascidians. There is debate over whether supplementation is necessary above levels encountered from incidental addition.
Major Sources: Aquarium additives, impurity in aquarium additives/salts
Concern: **Low.** Read More
Removal: Water changes, discontinuation of additives containting V

Tungsten (W): There is no scientific data on the toxicity of Tungsten in reef ecosystems.
Major Sources: Environmental
Concern: **Low.**
Removal: Water changes

Zinc (Zn): Zinc is critical in the transmission of genetic information as well as protein production. While zinc is an essential element to coral health (for key enzymes), elevated levels of zinc can cause corals harm.
Major Sources: Foods, aquarium additives, exposed metal in aquariums, magnets, impurity in aquarium additives/salts
Concern: **Low.** Toxicity at 0.1 ppm Read More
Removal: Water changes, discontinuation of additives containing Zn