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A Basic Guide to the Chemistry of Marine Aquariums

The Cyclic Chemistry of Marine Aquaria
And Biosystems

Gerald Jennings



Basic Guide to the Chemistry of Marine Aquariums

The Cyclic Chemistry of Marine Aquaria and Biosystems

A Guide as to why your marine system can go wrong and where it can go wrong, and possibly what to do to stop it going wrong.

It makes sense to buy this book before losing or killing expensive marine fishes

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Preface

Every year hundreds of thousands of marine fishes die as a result of ignorance. Many of these are newly acquired pets whose loving and caring owners unintentionally manage to terminate their lives ironically whilst trying to give them the best life possible.

There has always been little support they could call on. The trade in animals is, like any other trade, a cash cow, and few sellers will accept any responsibility once the purchased have left their care.

The "organized hobby" is now virtually toothless and non-existent - no longer are there many local experts and aquarium groups to turn to - and their successor, the

internet, is both impersonal and generally overly well stocked with rather poor advice. There are always exceptions of course.

The IFOCAS group is such an exception. It is dedicated to spreading accurate and wherever possible, free information, on fishkeeping worldwide.

IFOCAS have sponsored us in publishing this booklet which it is hoped will convey at least a little light in to the often murky waters of fishtank chemistry. We have tried to simplify a very technical subject so we ask the purists not to be offended. We are also able to offer free helplines for all enquiries on this matter, both simple and technical - just use one of the websites or email addresses listed below.

Calypso Publications. <http://www.calypso.org.uk> enquiries@calypso.org.uk

IFOCAS. The International Federation of Online Clubs and Aquatic Societies <http://www.ifocas.fsworld.co.uk> secretary@ifocas.fsworld.co.uk

IFOCAS is represented in all Continents

Introduction

A marine aquarium is an unnatural environment. In the sea, water conditions are basically constant, but in an aquarium water conditions are continually changing. Since aquatic organisms are in intimate contact with their environment, any change in the composition of the water has a profound effect on their well - being.

As an aquarist you must be able to recognize the condition of the water in your aquarium, and take appropriate action when water quality declines, as it inevitably will. Acquiring a basic understanding of water chemistry is an important step in becoming a more knowledgeable and, ultimately, a more successful marine aquarist.

It is possible to maintain and enjoy a marine aquarium with little or no concern for routine water analyses. In fact, many hobbyists are content with knowing that regular, partial water changes are sufficient to maintain adequate water quality in many situations. As long as such aquariums are not overcrowded or overfed, there is little reason to expect that water quality will deteriorate enough to be detrimental.

However, many marine enthusiasts are not content with simply maintaining decorative displays. Some are challenged to maintain particularly delicate fish and invertebrates. Others are spawning and rearing many popular species.

These aquarists need to know more about the water in their systems. Analysis of the water can greatly complement the information gained by careful observation of the aquarium inhabitants, and help establish guidelines for all future aquarists.

Seawater is a complex solution, and to accurately determine the concentrations of many components is difficult, time consuming, and costly. Fortunately, experience has shown that we can learn a great deal about aquarium environments by analyzing for a relatively small number of items.

Unfortunately, the marine aquarist wishing to consider water chemistry is often in an uncomfortable position. Bits and pieces of information are frequently gathered from various sources that can be both contradictory and inadequate.

This text attempts to fill some possible gaps in the reader's knowledge of water chemistry. It discusses the nature of seawater, and common water chemistry parameters with emphasis on the type and value of the information that can be obtained from a particular analysis.

To aid in understanding the following chapters, it is appropriate to define several terms before continuing. Additional definitions are also found in the glossary towards the end.

A little basic chemistry.....

The basic chemical unit is the atom. It is composed of three distinct small particles - protons, neutrons, and electrons

(The number of protons equals the number of electrons, and the identity of the atom is defined by the number of protons.)

Atoms are usually expressed in text as chemical symbols.

For example, Ca stands for calcium, and H stands for hydrogen.

Other symbols are based on Latin names, such as Na for sodium (Natrium) and K for potassium (Kalium).

Symbols are convenient and will be used frequently in the following text. Some of the commonly used symbols are shown below:

Common Chemicals and Symbols used

Hydrogen	H	Manganese	Mn	Silicon	Si
Lithium	Li	Iron	Fe	Nitrogen	N
Sodium	Na	Cobalt	Co	Phosphorous	P
Potassium	K	Nickel	Ni	Oxygen	O
Rubidium	Rb	Copper	Cu	Sulphur	S
Magnesium	Mg	Zinc	Zn	Fluorine	F
Calcium	Ca	Boron	B	Chlorine	Cl
Strontium	Sr	Aluminium	Al	Bromine	Br
Barium	Ba	Carbon	C	Iodine	I
Vanadium	V				

A collection of identical atoms is called an element. For example, sodium is an element. A piece of pure sodium consists of only sodium atoms, and they cannot be changed to atoms of any other elements. They will always be sodium atoms. However, they are capable of reacting or combining with atoms of other elements to form new materials called molecules. **A molecule is a collection of two or more different types of atoms connected by chemical bonds.**

(If sodium, a soft, silvery metal, reacts with chlorine, a greenish-yellow gas, sodium chloride (common salt), is formed. The substance formed is not similar to either of the components.)

Ions are electrically charged particles. They possess an excess of electrons (negatively charged) or a deficiency of electrons (positively charged). **Some molecules form ions when they are dissolved in water.**

Sodium chloride (NaCl), dissolved in water, produces positively charged sodium ions (Na⁺) and negatively charged chloride ions (Cl⁻)

(a) A Sodium chloride molecule forms a *positively* charged sodium ion and a *negatively* charged chloride ion.

Whereas

(b) A Potassium nitrate molecule forms a *positively* charged potassium ion and a *negatively* charged nitrate ion.

Ions can be either atoms, like sodium, potassium and chloride, or molecules, like nitrate

If both sodium chloride and potassium nitrate are dissolved in the same solution, it is impossible to tell what the original compounds were. Dissolving potassium chloride and sodium nitrate produces the same result). It is often difficult to represent the components of complex solutions as neutral (uncharged) compounds. **For this reason, the composition of natural seawater is given by concentrations of elements, such as sodium and magnesium, or ions, such as nitrate, rather than as concentrations of compounds, such as sodium chloride, magnesium sulphate, or sodium nitrate,** so identical solutions can be obtained by dissolving various combinations of different compounds.

**TECHNICAL BIT – SKIP THE NEXT FEW PARAGRAPHS
IF YOU NEED TO**

Elements or molecules in seawater are usually shown as concentrations by volume or weight in solution. Modern literature uses the metric units of weight per volume, milligrams per liter (mg/l). Parts per million (ppm) is more popular in non-technical literature. The two terms, although different, are often used interchangeably.

Many elements occur in solution as free ions, such as sodium (Na⁺) or chloride (Cl⁻); and it is convenient to simply report the concentrations of the elements (e.g., 10,500 mg/l Na⁺).

Other elements occur as components of molecular ions, such as nitrate (NO₃⁻) or phosphate (PO₄⁻⁻); and it is more convenient to report concentrations in terms of the element of interest.

For ammonia (NH₃), nitrite (NO₂⁻), and nitrate (NO₃⁻), concentrations are reported as milligrams per litre of ammonia-nitrogen (NH₃-N), nitrite-nitrogen (NO₂--N), and nitrate-nitrogen (NO₃--N). Similarly, for phosphate, phosphorous is reported (P₀₄--P).

This system permits easy, direct conversion. For example, 10 mg/l NH₃-N will produce 10 mg/l NO₂--N and ultimately 10 mg/l NO₃--N. When reading other books or articles, it is important to know which system is in use. To convert mg/l NH₃-N to mg/l NH₃, multiply by 1.3; to convert mg/l NO₂--N to mg/l NO₂⁻(ion), multiply by 3.3; to convert mg/l NO₃--N to mg/l NO₃⁻(ion), multiply by 4.4.

Numbers in the latter system are always higher because they take in to consideration the contribution of the hydrogen and oxygen to the molecular weight. For example, 10 mg/l nitrite-nitrogen equals 33 mg/l nitrite ion, but both numbers represent the same concentration of nitrite. It's similar to your thermometer saying that the temperature is 75 degrees Fahrenheit or 25 degrees Celsius. You know that, although the numbers are different, the temperature is still virtually the same.

The Seawater Itself

(A.) Natural Seawaters

Seawater is a solution containing approximately 34 parts per thousand of dissolved materials. Many oceanographers have conducted determinations of the composition of seawater throughout the world and all results are extremely constant with only a few well-known area exceptions.

An examination of record tables shows that seawater contains most chemical elements, many at extremely low concentrations. However, in our discussion of aquarium water chemistry,

only a few of these elements are critically important.

MAJOR COMPONENTS

The major ionic components of seawater are the same as the ions responsible for maintaining electrical and osmotic balance within the cells of living animals and for transmission of nerve impulses.

The complete absence of any one of these major ions is fatal. A fish placed into a modified seawater solution that contained no potassium would soon die as a result of the chemical imbalance within the animal.

The "Biggest Six" Major Ions Found In Seawater

Component	Concentration (mg/l)
Chloride	19,000
Sodium	10,500
Sulphate	2,600
Magnesium	1,350
Calcium	400
Potassium	380

The major components vary little. It is accepted practice to represent these as either ratios to chlorinity.** or milligrams per litre as shown above

** Chlorinity. For definition see glossary.

The ratios for nine major ions are listed below together with any natural variations.

Sodium. (Na⁺) .556±.0003

Calcium.(Ca⁺⁺) .0210±.0005

Magnesium. (Mg⁺⁺) .0671±.0005

Potassium. (K⁺) .0200±.0005

Strontium. (Sr⁺⁺) .00060±.00015

Chlorine as chloride (Cl⁻) 1.0

Sulphur as sulphate (SO₄) 1395±.0005

Bromine as bromide, (Br) 00~3±.0001

Boron as H₃BO₃. 00134±.00005

(Bicarbonate, carbonate & CO₂ contents are variable.)

The above ratios are all taken from modern analyses. Older figures may differ.

There are very few natural exceptions to the above ratios, and most of these when they occur

are extremely localised. Those that may be of significance are :

Magnesium: Slightly higher ratios are recorded for the Gulf of Aden and the eastern Mediterranean, being .0681 and .0688 respectively.

Calcium: Most records prior to about 1938 have to be recalculated as they include Strontium readings.

Strontium: (See remark on calcium above). Strontium is used by many radiolarians and is heavily adsorbed by diatoms and red and green algae.

Boron: Ratios increase in the deep Pacific and may exceed .00162 It is used by many marine plants and contributes to the basicity discussed later under pH

The major ions are an area of little concern to most fully marine, as opposed to brackish-water aquarists. Preparations of synthetic seawater always attempt to duplicate the concentrations of the major ions of natural seawater, and this can be accomplished with many different combinations or recipes of chemical compounds. Since the major ions can be obtained from readily available chemical raw materials, it is probably safe to assume that all commercial formulations of synthetic sea salts have succeeded in duplicating, at least, this part of the sea.

THE MINOR CONSTITUENTS

The minor ions present in seawater exert an influence far greater than their concentrations suggest. They represent less than half of one percent of the total, most of which is silicate or fluoride and vary considerably from season to season and area to area. Of the 67 so far identified approximately 24 are either known or thought to be of some biological importance. Of the remaining 33 little information is available, save for the occasional research paper, though it is known that some occur in remarkably stable concentrations in all open ocean waters. Six of these are included in a table later in addition to the eighteen of biological interest listed. Much more research into other microconstituents is needed.

As has already been mentioned the concentrations of some of these traces do vary (for a number of reasons), and this has to be taken into consideration in any assessment of water condition. Most earlier types of synthetic waters were based on minor constituent readings taken from waters around the coasts of temperate continents, and are not accurate for the central areas of larger water masses- these being in general much poorer in nutrients such as phosphate, nitrate and iron than their continental counterparts.

TABLE TWO.

<u>RECORDED</u>	<u>MINOR</u>	<u>CONSTITUENTS</u>
Silicon	Antimony	Dysprosium
Fluorine	Beryllium	Erbium
Nitrogen (NO ₃)	Bismuth	Europaeum
Lithium	Cadmium	Gadolineum
Rubidium	Caesium	Hafnium
Iodine	Cerium	Holmium
Phosphorus (PO ₄)	Chromium	Lutetium
Barium	Gallium	Neodymium
Iron	Germanium	Praesodymium
Molybdenum	Indium	Protoactinium
Zinc	Lanthanum	Rhenium
Selenium	Krypton	Samarium
Manganese	Lead	Terbium
Vanadium	Mercury	Tantalum
Nickel	Radium	Ytterbium
Uranium	Ruthenium	
Aluminium	Silver	
Arsenic	Thallium	Argon
Copper	Thorium	Deuterium
Cobalt	Tin	Helium
Niobium	Titanium	Neon
Yttrium	Tungsten	Radon
B12	Zirconium	
Gold		

Some microconstituents, notably nitrate, nitrite and ammonia, which occur naturally in ocean waters, are probably unnecessary additions to any synthetic formulation, unless it is to be used solely for plants and algae. These are formed quite quickly in waters by the metabolic activity of higher animals, and indeed this process can cause dangers in small closed circuit systems. It is notable that open ocean waters and tropical reef waters seem to contain much

less. Results have been published -some very recently- on the following relationships.

Lithium-Rubidium, Strontium-Calcium, Phosphate-Arsenate, Copper – Zinc, and many more, a full list of which is not practicable here.

Some of the ratios are of greater importance than others and are useful in the comparison of waters

CARBON DIOXIDE CONTENT / pH*

If in addition to its salinity and temperature (from which its SG -or specific gravity can be calculated) the pH is known, then its content of bicarbonate, carbonate, molecular carbon dioxide & total carbon dioxide can be calculated. *(NB. This does not apply to synthetic formulations)* The total carbon dioxide present in solution varies almost in direct proportion to salinity. If 35 parts per thousand water at 15 deg. C. is brought into equilibrium with the atmosphere it will show a pH of about 8.16, which is increased by the growth of any plants and decreased by the respiration of animals.

Bicarbonate is most important because it is the ion primarily responsible for buffering, or maintenance of pH. Borate also provides some contribution to the buffer system, but its effect in natural waters is small in comparison. (The subject of pH will be discussed in a subsequent chapter).

The importance of the remaining minor ions is less obvious. Silicate is essential to certain algae, and perhaps some animals. Bromide and Strontium, however, have more complex relationships. It is likely that the complete absence of either would have little effect on the health of most, but not all, aquatic organisms.

Trace elements

Trace elements are those ions that are normally encountered at concentrations near or below 1.0 mg/l

The term **trace element** refers only to the fact that the element is present in **trace** quantities. The term as applied does not itself imply any degree of importance with regard to the health of aquatic organisms.

Many aquarists fail to differentiate between trace elements and essential elements. They are two distinct groups. Not all trace elements are essential, though the long-term absence of some within a system has yet to be assessed

Trace Elements

CONSTITUENT KEY	CONCENTRATIONS IN MICROGRAMS PER LITRE
Silicon (1)	500-2,900
Fluorine (2)	1.350+/- 50
Nitrogen as N03 (1)	600+/-100
Lithium (2)	170+/- 30
Rubidium (2)	120+/- 10
Iodine (1)	55+/- 10
Phosphorus as P0+ (1)	1 to 90
Barium (1)	6 to 90
Iron (1)	1 to 40
Molybdenum (1)	9 to 16
Zinc (1)	5 to 21
Selenium (2)	5+/- 1
Manganese (1)	0.4 to 10
Vanadium (1)	0.2 to 7
(1) Components of proven or suspected biological activity	
Nickel (1)	0.5 to 6.6
Strontium (2)	2.5 to 3.3
Aluminium (2)	1 to 5
(2) Components of known ratio stability	
Copper (1)	2.4+/- 0.3
Cobalt (1)	0.9 to 3
Nickel (1)	0.1 to 0.7
Yttrium (1)	0.01 to 0.3

Figures given are taken from various published statistical handbooks the latest available for open oceanic waters unaffected by land drainage or other sources. The table above is also representative of many tropical reef waters .

There is no biological process that depends on the presence of all of those above. Even though they are trace elements normally encountered in natural ocean water, they are probably not essential elements. Many trace elements are not essential chemical elements according to present-day information.

Many of the trace elements that are essential are heavy metals (e.g., Chromium, Manganese, Iron, Cobalt, Copper, and Zinc). Their importance to living organisms depends on the ability to interact with various organic molecules, such as enzymes, and form stable complexes with specific biological functions.

Water in an established aquarium contains significant quantities of dissolved compounds that may also be capable of forming stable complexes that make the metallic elements unavailable. Additionally, these complexes are readily removed from solution by activated carbon and other adsorbents.

Even in the absence of organic molecules and adsorbents, these elements may form insoluble

inorganic compounds, such as carbonates, or hydroxides which precipitate from solution. All these various mechanisms combine to make the aquarium water an unreliable source of many essential trace elements.

The problem of supplying essential trace elements is not one of water chemistry, it is one of nutrition. It is reasonable to expect that higher animals should obtain essential nutrients, including trace elements, from the food they eat. The best method of insuring that your animals receive these nutrients that they require is to provide a varied diet of high quality foods.

The Seawater Itself

(B) Synthetic Seawaters

THE BASIC CHEMISTRY OF SYNTHETIC SEAWATER

The major salts used in formulation correspond approximately to the major constituents of ocean water shown .to ascertain how large a quantity of salt may be required it is usual practice to convert the natural readings, into gram-equivalents, from their original grams per kilo quantities as shown on the Table. This process is best described by giving an example of the technique.

Column (a) of Table 1 shows the weights of nine final elements required. Gram per kilogram weights are then divided by the atomic weight of each element concerned to convert them into gram-equivalent weights. eg;-

The weight of element in seawater divided by the Atomic weight of the same element = the Gram-Equivalents weight.

PERCENTAGE COMPOSITIONS				GRAMS PER KILO		
(1)	(2)	(3)	(4)		(A)	(B)
30.4%	30.63%	30.59%	30.61%	SODIUM	10.71	10.77
3.7	3.70	3.63	3.69	MAGNESIUM	1.29	1.30
1.16	1.16	1.15	1.16	CALCIUM	0.406	0.409
1.1	1.10	1.105	1.10	POTASSIUM	0.386	0.388
0.04	0.028	-	0.04	STRONTIUM	0.013	0.010
55.2	55.18	54.95	55.05	CHLORIDE	19.26	19.37
7.7	7.7	7.7	7.7	SULPHATE	2.69	2.71
0.19	0.185	0.188	0.190	BROMIDE	0.066	0.065
0.07	0.074	0.074	0.07	H BO	0.026	0.026
to	to	to	to	BICARBONATE	to	to
100%	100%	100%	100%	CARBONATE & OTHERS	35	35

The table above assumes a salinity of 35 parts per thousand

(1) Data recalculated, using 1940 atomic weights, from Dittmar. This recalculation allowed for Strontium. (Lyman & Fleming)

(2) Figures published 1954-1960. (Various sources)

(3) From figures published 1968. Recalculated 1973.

(4) Figures published 1969. (Orr & Marshall)

(A) From figures published 1969 (Orr & Marshall). Recalculated and adjusted to a salinity of 35. Calypso Research 1977.

(B) Devised from many analyses. (Harvey 1966)

Most manufacturers of laboratory chemicals state the molecular weight of a reagent or salt on its packaging and labels, if not also in their catalogues. A simple multiplication will then provide a working result as:-

Gram-Equivalent weight x Molecular weight = Final weight of salt needed.

(The mathematics involved also of course work in reverse, and formulae stating weights of salts can be converted back into weights of elements per kilo and then compared to Table 1.)

It is imperative that if a formula is being worked out, one works in reverse order, dealing first with the minor constituents, then on up into the major constituents to the penultimate figure, the one for Sodium chloride. The salt containing bicarbonate is the last to be calculated, enough HCO ions (theoretically) being added to use any spare sodium ions as yet unpaired in the formulation, remembering that any ion carrying a positive (+) indicator has to be paired with a similar ion carrying a (-) negative indicator, and that where an ion carries two symbols of one type, it requires double the quantity of an opposite type carrying only one symbol. (eg. Na⁺ plus Cl⁻ = NaCl, which is common salt but Na⁺ plus SO₄⁻⁻ = Na₂SO₄, or sodium sulphate.

Thus only ten gram equivalents of chlorine (Cl) are needed to neutralise ten gram-equivalents of sodium in the first example but twenty gram-equivalents of sodium would be used in neutralising ten gram-equivalents of sulphate in the second.

INTRODUCTION TO SYNTHETIC SEAWATERS

In the preparation of this text we have incorporated as much modern data as possible. The synthesis of artificial seawater itself dates back some 150 years, and since the voyage of

"HMS Challenger" and Ditmar's subsequent publication of its findings formulae have been proposed that simulate natural seawater.

There are many reasons for wanting to synthetically produce a substance which in nature covers over seven-tenths of our native planet, but undoubtedly the major one for biologists, aquarists and aquarium managers everywhere is convenience.

Approximately ninety six percent of seawater is water, only the remainder being salts, and transportation of any bulk liquid is both tedious and expensive. Even assuming that one is willing and able to undertake the collection of one's own seawater there are problems:-

(1) If collected close on-shore it may be polluted - a fact that is often not immediately obvious but may often result in later losses of stock.

(2) The waters of the European and North Atlantic (or indeed any Continental shelves - which include most off-shore areas around our coasts) differ in many respects both from oceanic waters and to those present in tropical seas.

In these times of 'Convenience Products' it is far simpler to think in terms of a 'Convenience Seawater', - one either made from easily obtainable laboratory chemicals, or pre-package salt mixes from your local aquarium supply shop. and then - Hey Presto - a breed of "instant seawater" How good it will be depends entirely on the scrupulousness of the manufacturer.

Is it the nearest possible synthesis, or just a mixture designed to keep things going for a while ?

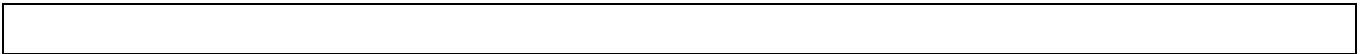
For those about to become interested in the field we have included a large number of pages in the text devoted to various aspects of this discussion and for those dedicated chemists who wish to construct their own " perfect seawater" a note - it has already been done. The formula can be found in one of the Appendices at the rear. Notwithstanding this, we hope that this book will even appeal to those who are apprehensive even at the mention of the word chemistry. We make no apologies for its simplicity, and wherever possible it uses non-technical and very easy-to-understand terms. For those already interested we have included a bibliography.

Way back in 1979 the team at Calypso Research in the UK published what is probably the definitive work on "Synthetic Seawaters" and keen readers are urged to request a copy from them if required. The text of their report proper covers an assessment of nine formulae for synthesizing seawaters. Some of these are old, some are relatively modern, and one is as yet unpublished in the marine biological paper for which it was intended . All of these nine formulae are in everyday use, some throughout the world, others only in the U.K. and Europe. Many of them have been commercially marketed under an assortment of trade names, either in their original form, or as a modification, Some of the marketed products have been 'modified' for use in tropical marine aquaria. Where permission has been given either by precedent or in writing, the names under which the formulae discussed have been marketed are given in the report text.

The following are some of the trade names under which the examined salts have been marketed for aquarium use. Legal protection exists in all cases.

'Aqua-Sea', Dr.Axelrod's Formula, 'C-Water', Meereswasser, 'Instant Ocean', Marina, H.W.Meeressalz , Rila Marine Mix, Reef Salts, 'Synthetica', 'Tropic-Marin', 'Triton Marine TM Salts',

This list is not comprehensive and not all of these thirteen formulae have been examined,



Feeding in relation to microconstituents

Feeding a variety of foods is the best means of meeting nutritional requirements

Commercial aquarists have realized this for some time, and commercial fish foods contain supplemental quantities of essential micro-nutrients. This attitude is now being seen at the hobbyist level, and many similar foods for ornamental fish are now available.

If higher animals are your primary concern, there should be no need to add supplements to the aquarium water. However, if plants (algae) are a primary interest, the situation is different, because plants do not "eat" and must obtain their nutrients by direct absorption from the water.

Most aquariums that contain fish are also capable of supporting a modest growth of algae, because the waste products of the fish provide sufficient nutrients. However, for intensive algae culture, supplements are always necessary to restore nutrients that have been depleted from solution.

As interest in spawning marine fish grows, intensive algae culture is gaining increasing attention among marine hobbyists. It often becomes necessary to produce quantities of micro-algae which are, in turn, used to culture food for newly hatched larval fish. Useful algal growth supplements are commercially available, or may be prepared from one of numerous published formulae.

Algae are on the bottom of the food chain in nature; and it is likely that many of the nutrients that they absorb from solution ultimately supply the higher animals.

The Chemical Environment

If one examines analyses of seawater, two important points are evident. First, proportions of all the major elements are remarkably consistent throughout the world as has been demonstrated in previous paragraphs. This is fortunate because it allows us to mix organisms that are native to many different locations.

Secondly, concentrations of inorganic nutrients (nitrogen as ammonia, nitrite and nitrate, and phosphorous as phosphate) and dissolved organic matter are quite low. **This is a major**

chemical difference between seawater in the ocean and seawater in an aquarium.

Accumulations of these inorganic components is a characteristic of closed system aquariums and must be controlled by proper maintenance and filtration.

The following chapters discuss various water quality parameters that you are capable of controlling, and, in fact, must control. With a few unsophisticated accessories you can monitor a-number of important factors and take appropriate action when necessary.

Salinity

Variations in naturally recorded salinities are small. With the exception of areas such as the Baltic, which is extremely low in dissolved salt the regions immediately adjacent to melting polar ice, and certain localities in the Red Sea it rarely exceeds 38 parts per thousand and is normally not less than 33 parts per thousand. Nine major ions constitute in excess of 90% of these readings. The salinity value was originally obtained by titration but more modern estimations are usually made by methods using a range of techniques; electrical conductivity, its refractive index, density, or the velocity of transmitted sound signals.

Salinity is a measurement that indicates the amount of salts dissolved in water. Concentrations are commonly expressed as parts per thousand (ppt or ‰). Normal seawater salinity is 34 parts per thousand, meaning that 1,000 grams of seawater contains 34 grams of dissolved salts.

Marine aquariums are usually maintained at salinities slightly lower than natural sea water, commonly 27 to 31 parts per thousand. This lower salinity benefits fish by requiring less energy to maintain osmotic balance.

Aquarists ordinarily determine salinity indirectly by measuring specific gravity, which is a comparison of the density of a solution at a specified temperature (usually 15°C) to the density of pure water at a specified temperature (usually 4°C). A specific gravity of 1.100 means that at 15°C, the solution being measured is 1.100 times denser than pure water at 4°C.

Specific Gravity	Salinity parts per thousand
1.015	20.8
1.016	22.0
1.017	23.3
1.018	24.6
1.019	25.9
1.020	27.2
1.021	28.5
1.022	29.8
1.023	31.1
1.024	32.4
1.025	33.7
1.026	35.0
1.027	36.3
1.028	37.6

Changes in the amount of salt dissolved in the water affect the specific gravity in a predictable and directly related manner. Therefore, every salinity reading will have a corresponding specific gravity. If the specific gravity is known, the salinity can be found by using conversion tables.

Specific Gravity (SG) is conveniently measured by use of a hydrometer, Higher specific gravities cause the indicators to float higher in the solution. - lower specific gravities cause them to float lower. For ease of use, a hydrometer should be calibrated at a temperature near that of the water being tested. Most high quality aquarium hydrometers are calibrated for use at 75°F. Hydrometers calibrated at significantly different temperatures, such as 60°F, require corrections to obtain the actual specific gravity.

For most marine aquariums at 75°F a reasonable estimate of salinity can be obtained by taking the last two digits of the specific gravity reading and multiplying by 1.35. (Example:

Specific Gravity 1.020. Multiply 20 x 1.35 = 27 -ppt for estimated salinity).

In actual practice, most hobbyists dispense with the use of salinity and simply refer to the specific gravity. The range 1.020 to 1.023 is most common.

pH

Most aquarists, freshwater and saltwater alike, begin their education in water chemistry when they are introduced to pH testing. The earliest aquarists realized the importance of proper pH, and an understanding of elementary concepts of pH will aid in understanding subsequent topics. (Keep in mind that pH is a complicated subject and that the following is greatly simplified).

Principles of pH

Water is composed of two elements, hydrogen and oxygen. In a molecule of water, two hydrogen atoms are bound to a central oxygen atom (Fig. 5a). In a volume of water, some of the molecules dissociate, or separate, into hydrogen ions (H⁺) and hydroxide ions (OH⁻). The pH represents the concentration of the hydrogen ions.

Lower numbers on the pH scale represent higher hydrogen ion concentrations, and each pH unit denotes a tenfold change in concentration. That is, at pH 6, there are 10 times more hydrogen ions than at pH 7; at pH 8, there are 1/10 the number of hydrogen ions at pH 7.

When the number of hydrogen ions equals the number of hydroxide ions, the hydrogen ion concentration is represented by pH 7; and the solution is neutral. If the hydrogen ion concentration is increased, the pH falls below 7, and the solution is acidic. Conversely, if the hydrogen ion concentration is decreased, the pH rises above 7, and the solution is alkaline.

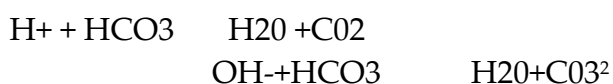
pH can be changed by addition of substances that affect the hydrogen ion concentration. Hydrochloric acid (HCl) dissociates into hydrogen ions (H⁺) and chloride ions (Cl⁻). When added to a solution, there will be an increase in the overall hydrogen ion concentration and pH will drop.

It's easy to visualize that adding more hydrogen ions increases their concentration and lowers pH, but how is the hydrogen ion concentration lowered to increase pH? Obviously, one cannot reach into a solution and selectively pull out the hydrogen ions.

The hydrogen ion concentration and the hydroxide ion (OH⁻) concentration are related. When one increases, the other decreases. Adding a substance that increases the hydroxide ion concentration lowers the hydrogen ion concentration. Sodium hydroxide (NaOH) dissociates into sodium ions (Na⁺) and hydroxide ions (OH⁻). Addition to a solution increases the hydroxide ion concentration and, consequently, decreases the hydrogen ion concentration, resulting in a higher pH.

Many substances affect pH when added to an aqueous solution. Some contain neither hydrogen ions nor hydroxide ions, but affect the pH indirectly.

Sodium bicarbonate dissociates into sodium ions (Na⁺) and bicarbonate ions (HCO₃⁻). Solutions of sodium bicarbonate are slightly alkaline and have a pH near 8.4. Additions of small amounts of strong acids or bases (alkalies) to solutions of sodium bicarbonate do not produce the expected change in pH because the hydrogen ions (H⁺) or hydroxide ions (OH⁻) are neutralized by the bicarbonate:



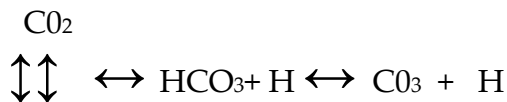
Unlike acids and bases, solutions of sodium bicarbonate have a relatively constant pH over a wide range of concentrations.

pH , Excess Basicity , & the CO₂ System

Natural seawater is alkaline in nature due to its containing an excess of basic (+) over acidic (-) ions. This 'excess basicity' is attributable to bicarbonate (HCO₃), carbonate (CO₃), borate (H₂B₀₃) carbon dioxide(CO₂) and carbonic acid (H₂C₀₃). All exist in equilibrium with each other and with the hydrogen ions (H) present. It is a self-balancing system, and as such natural variations are exceedingly small and rarely exceed the pH range of 8.0 to 8.3. If one of these variables is altered the complete system changes and a new state of equilibrium is attained quite rapidly, This change is effected by several mechanisms related to these constituents

(1) If the pH increases boric acid (H₃B₀₃) changes to H₂B₀₃+ H⁻ , so releasing a hydrogen ion to inter-react with the carbon dioxide system

(2) The carbon dioxide system (graphically illustrated below) *



H₂C₀₃

adjusts itself until a new state of equilibrium is reached. This also entails the inter-reaction of atmospheric carbon dioxide though this takes place relatively slowly.

These mechanisms have been studied thoroughly and very accurate estimates are possible for the reacting components.

The term pH is used as an expression of the hydrogen ion concentration, and as such this is measurable easily and quite accurately. **In natural waters this gives an accurate representation of the 'status quo' but this is not the case with many synthetic formulations especially those which omit boric acid or a boron salt, or those that increase the quantity of sodium bicarbonate. In either of the above two cases the pH reading will not give a representative indication of the condition of the carbon dioxide system, and the speed of any equilibrium correction may be affected.**

pH READINGS

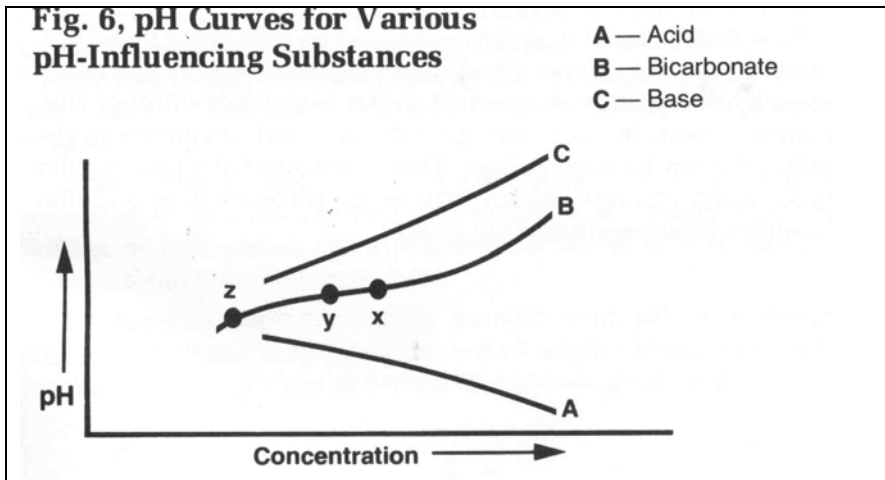
The hydrogen-ion concentration of aquarium and laboratory water is often measured using colorimetric comparison methods. Dangers occur here : -

(1) See above paragraph relating pH to components used in any synthetic formulation.

(2) Normal Freshwater Colorimetric indicators are subject to ' salt error' and have to be

corrected for use in sea water, unless specifically designed for marine use

Fig. 6, pH Curves for Various pH-Influencing Substances



Consider a solution represented by point x on curve B. If hydrogen ions are now added to the solution, what happens? The hydrogen ions react with the bicarbonate and are neutralized. The bicarbonate concentration is decreased to point B, but we are in a region of the curve where a change in bicarbonate concentration results in little change in pH. Consequently, pH remains relatively unchanged in point y. From the curve, it is obvious that pH will remain relatively constant over a range of bicarbonate concentrations. This is the principle of buffering, or stabilization of pH.

Many chemicals can be used to prepare buffered solutions. In a marine aquarium, bicarbonate is the principal ion responsible for stabilization of pH. Biological action produces acidic substances that are subsequently neutralized. Continued addition of acid depletes the buffer, which must eventually be replenished or a dangerous drop in pH may result [Point z].

The capacity of a system to neutralize additions of acid is represented by a property called alkalinity. A solution with high alkalinity is relatively insensitive to moderate additions of acidic

materials, whereas a solution with low alkalinity may experience a significant drop in pH under similar circumstances.

Proper pH is essential because availability of hydrogen ions is important to many biochemical reactions within living cells.

Buffers can help to maintain a proper pH in the aquarium

Small changes in pH can profoundly affect these reactions. Remember a change of one pH unit means a tenfold change in hydrogen ion concentration.

The pH in a marine aquarium should be between 8.0 and 8.4, with 8.1 - 8.3 considered ideal. The pH

and alkalinity are maintained by buffers that are present in the initial salt solution, and, to some extent, by carbonate gravel and coral. As buffer is depleted, it must be replenished. This is accomplished by regular partial water changes, which may be supplemented by careful addition of Sodium (bicarbonate of soda) or Potassium bicarbonate.

I

Oxygen and Carbon dioxide

Sufficient oxygen (O_2) is essential to marine aquariums. A warm water marine aquarium contains approximately 7 mg/l O_2 at saturation, and the oxygen concentration should always be maintained near saturation.

Fortunately, all that is necessary to accomplish this is vigorous aeration and circulation of the aquarium water. Gas exchange takes place at the air-water interface. Oxygen dissolves into the water to replenish that which has been used.

Animals (and plants in the dark) utilize oxygen to produce energy. In the process, carbon dioxide (CO_2) is produced, and released to the water.

Removal of carbon dioxide is as important as replacement of oxygen. If carbon dioxide builds up in the aquarium water, it becomes more difficult for fish to release it from their blood through the gills. Excessive carbon dioxide in the blood lowers its pH, which decreases the capacity for carrying oxygen. In extreme cases, fish can suffocate even in the presence of excess oxygen.

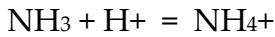
In seawater with a safe pH (above 8), carbon dioxide is converted to bicarbonate (HCO_3^-). At lower pH values the proportion of free carbon dioxide increases. Some of this may be slowly released to the atmosphere.

If aquariums are adequately aerated, and pH is properly maintained, there is little likelihood of encountering problems due to oxygen depletion or carbon dioxide accumulation.

Inorganic Nitrogen

Marine animals produce ammonia as a metabolic waste. Additionally, ammonia may be produced by bacterial action on uneaten food and other matter. The input of ammonia into aquarium water is constant, and ammonia is toxic to marine animals.

Ammonia in solution exists in two chemical forms, unionized (NH_3) and ionized (NH_4^+) which considered together are referred to as total ammonia. Ionized ammonia is formed by reaction of un-ionized ammonia with a hydrogen ion (H^+):



The proportion of ionized ammonia depends primarily on the availability of hydrogen ions, and is a function of temperature, salinity, and pH.

The strong influence of pH is easily understood when one recalls that pH is actually a measurement of the hydrogen ion concentration. In fact, because most aquariums operate within a narrow range of temperature and salinity, the contribution of these factors is insignificant.

Ammonia Equilibrium at Different pH Values at 22°C.

pH	7.8	7.9	8.0	8.1	8.2	8.3	8.4	8.5
% Ionized	97.7	97.1	96.4	95.5	94.4	93.1	91.4	89.5
% Un-Ionized	2.3	2.9	3.6	4.5	5.6	6.9	8.6	10.5

Equivalent amounts of total ammonia are more toxic at higher pH values. The Table shows that at the pH values normally encountered in a marine aquarium (pH 8.0 - 8.4), a significant proportion (4 - 10%) of the ammonia is un-ionized.

It has long been suggested that un-ionized ammonia is the toxic form, and that increased toxicity at higher pH values is due to increased amounts of un-ionized ammonia. It is also possible that ammonia is toxic in both forms, that higher pH values increase the toxicity of both forms, and that the increase in unionized ammonia is coincidental.

So little is known about the exact mechanisms of ammonia toxicity that neither explanation has yet been proven scientifically. It cannot be denied, however, that ammonia is toxic and its presence in an aquarium is detrimental.

Fortunately, ammonia does not accumulate indefinitely. Certain bacteria obtain energy by oxidizing it and, in so doing, convert it to a less toxic molecule, nitrite (NO₂⁻)

Although less toxic than ammonia, nitrite is still dangerous. It affects the haemoglobin in the blood, making it less capable of transporting oxygen. At worst, this can result in death. At best, the animal is still subjected to stress from which it may or may not recover completely.

Results of recent research suggest that nitrite may not be nearly as toxic to some saltwater animals as was previously suspected. Unfortunately, this has not been demonstrated conclusively for the marine animals found in most aquariums and, until such time, any prolonged exposure to nitrite ions should be regarded as unsafe.

Nitrite, however, like ammonia, is susceptible to bacterial action, which converts it to relatively harmless nitrate ions (NO_3^-). The process by which ammonia is converted to nitrite, and subsequently nitrate, is called nitrification.

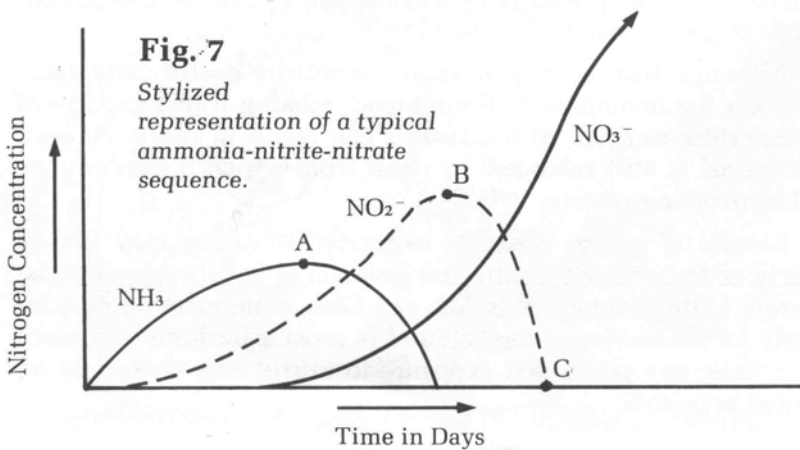
Conditioning

The initial establishment of nitrifying bacteria is called conditioning. It is normally approached by the early addition of one or two hardy animals to provide an ammonia source, and then allowing sufficient time for bacteria to multiply.

In newly set-up aquariums, ammonia accumulates as a result of the continuous input of animal wastes. Bacteria that utilize ammonia multiply and eventually the ammonia is oxidized to nitrite as quickly as it is produced. As nitrite forms it, too, accumulates until the bacteria that utilize it have multiplied sufficiently. Only nitrate continues to accumulate. The Chart below shows a classic sequence.

During conditioning, ammonia increases, usually for a period of 1-2 weeks, ordinarily reaching a maximum concentration of 3-6 mg/l $\text{NH}_3\text{-N}$ (Point A, Figure Below). The level then decreases as populations of bacteria become established. After 3 to 4 weeks ammonia should be virtually undetectable.

Nitrite appears shortly after ammonia. A maximum concentration is usually encountered in 2-4 weeks (Point B, Fig. 7), eventually decreasing to zero in 3-6 weeks (Point C, Figure Below). This



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signals the completion of conditioning and the point at which additional animals can be safely introduced.

Addition of more animals occasionally produces a modest increase in ammonia and nitrite, as bacteria equilibrate to accommodate the increased load. These changes should be temporary and subside quickly.

The conditioning period may be considerably shortened or eliminated completely by "seeding" a new aquarium with gravel from an older well established system. Using 10% of

conditioned gravel will permit much more rapid increases in population than would otherwise be possible.

Phosphorous

Phosphorous is encountered in the aquarium principally as dissolved phosphate (PO_4^{--}). Animal wastes are the primary source. Phosphorous concentrations increase as the water ages, but eventually level off. Maximum concentrations seldom exceed 3-6 mg/l (PO_4^{--})-P. No direct toxicity problems have been associated with, phosphate, and its presence in small quantities is of little concern but uncontrolled increases can result in algal blooms, followed by their subsequent disastrous collapses.

Phosphorous is an essential nutrient for algae, and its absence will severely limit growth of aquatic plants. An aquarium containing animals will always have phosphorous far in excess of that required by the "casual" algae that may be present. However, there are occasions when intensive culture of algae is desirable, perhaps for use as a food for other organisms. In such cases, especially in the absence of animals, it is likely that phosphorous, as well as other essential plant nutrients, will be depleted, and it will be necessary to maintain growth by use of supplements.

Organic material

Presence of significant concentrations of organic matter is an important difference between ocean water and aquarium water.

In an aquarium, animal wastes, excess food and excretions of plants result in accumulations of organic materials that are never encountered in the ocean. These substances can have a profound effect on aquarium life.

Non-living organic matter, either dissolved or particulate, is usually apparent upon visual examination.

Dissolved Substances

High concentrations of dissolved organic compounds are identifiable by observation of two situations. Either the water becomes highly coloured, or the surface foams excessively when aerated. Frequently both occur simultaneously.

As aquarium water ages, it becomes increasingly yellow due to the presence of colored organic molecules. The condition is unsightly, but is controlled, to some extent, by regular partial water changes.

In some cases it is necessary to provide for additional means of removal. Activated carbon is frequently used for this purpose. Activated carbon in an auxiliary filter will usually keep the water sparkling clear, by adsorbing colored and other dissolved organic compounds.

Many organic compounds are surface active; they behave similarly to soap or detergents. Surface active compounds result in a persistent foam on the surface of the water. Surface active compounds are also conveniently removed by activated carbon, but an alternate method utilizes the foaming phenomenon.

A foam fractionator, or protein skimmer is a device that is designed to maximize the amount of foam produced, and continually remove it from the water surface. The foam forming components are effectively removed from solution.

A third alternative is use of ozone to chemically "consume" large organic molecules. Ozone is frequently used in conjunction with activated carbon or foam fractionators for maximum efficiency and safety (activated carbon neutralizes excess ozone).

Removal of organic matter is necessary not only for the sake of appearance, but for the health of the aquarium inhabitants as well. There is strong evidence to suggest that high organic levels interfere with normal growth and development of fish, and may contribute to increased susceptibility to disease. Also, bacteria utilize oxygen to consume biodegradable organic compounds. This, in effect, increases the bio-load on the system, thereby reducing the total stocking capacity of the system.

Particulate Matter (aka Detritus)

Particulate organic matter eventually accumulates in the filter bed/s as a fine, dust-like material called detritus. It is formed from solid wastes and from dissolved organic molecules that combine to form groups that are too large to remain in solution. Continued aggregation results in the highly visible detritus within the filter bed.

Detritus is of little concern unless it becomes so substantial that the flow of water through any filter bed is impeded. However, since its appearance is unsightly, it is usually removed.

The most common method of removal is physical; by gently "vacuuming" the gravel when water is being removed for a partial water change. Various mechanical devices are also available for cleaning the filter bed, and these may not require removal of the aquarium water to be effective.

If detritus removal is conducted on a regular basis, there is little likelihood of encountering problems associated with the cleaning. It should be noted, however, that the detritus has a high surface area that is available for growth of nitrifying bacteria. In fact, some of the nitrification capacity of the filter bed can be attributed to the bacteria upon the detritus particles.

If allowed to accumulate for an appreciable time (several months), a significant portion of the nitrifiers may be on the detritus. Its removal could result in a substantial decrease in biological filtration capacity. In an aquarium that is loaded near capacity, this could be disastrous.

An aquarium maintenance program should always include regular cleaning of the surface of the filter bed.

Copper

Copper is given special attention because it is extensively used as a medication for protozoan diseases of fish. Levels of copper, used for therapeutic purposes, are far in excess of those normally encountered in nature.

Elevated copper levels may be dangerous to fish and invertebrates, but copper has a long history of successful application when utilized properly. However, it is a heavy metal, and is subject to the same instabilities discussed previously in the Trace Element Section. This makes proper utilization difficult.

Copper treatment should be maintained within a safe, yet effective, therapeutic range (0.10-0.20 mg/l) for at least 10 days. When copper sulphate is used, the copper concentration decreases soon after addition to the aquarium water and the level must be maintained with additional copper sulphate.

An accurate copper test kit is valuable, but most aquarists rely on the chance that regular additions, according to manufacturer's recommendations, will be sufficient. When following recommendations for regular additions, the copper concentrations that result depends on numerous conditions that vary in different aquariums. The actual concentration that results may be useless, effective, toxic, or somewhere in between. Without an accurate analysis, it is impossible to be certain.

For this reason, it is always preferable to utilize a separate aquarium for treatments. To attempt treatment of a display tank with only one or two unhealthy specimens is flirting with disaster.

During treatment, do not filter with activated carbon, charcoal or other adsorbents. They remove copper quickly, and are, in fact, an excellent means of reducing the concentration in an emergency.

Never use copper based medications if invertebrates are present, unless the formulation specifically states that it is safe to do so.. Many are especially sensitive to it and may be killed.

Recently developed medications contain copper that has been reacted with an organic substance to produce compounds that are more stable in solution, and less toxic to fish. They are also less toxic to parasites, and higher copper concentrations, which vary with different products, are necessary to be effective. Their primary advantage is stability in solution. Once an effective therapeutic level has been established, subsequent additions are unnecessary or greatly reduced. Most are still conveniently removed by activated carbon or other adsorbents.

Water chemistry as a guide to aquarium maintenance

Testing may be used to help indicate the quality of water in the aquarium. However, testing, by itself, is neither beneficial nor detrimental to water quality, and is useless unless the aquarist is aware of appropriate action, and prepared to take it, when tests indicate that it is necessary.

The situations discussed here are those most frequently encountered: new aquariums, established aquariums, and hospital or medication tanks. A fourth situation, high density rearing or hatchery aquariums, is a specialized subject which warrants its own literature.

Conditioning of new aquariums

(Yes, you may have read this paragraph a little earlier, but we feel it's important enough to repeat.....)

In conditioning of new aquariums, a few hardy animals are introduced to provide a source of ammonia. Simply setting up the aquarium and letting it operate for several days without animals does absolutely nothing. Animals must be added to provide a source of ammonia for the nitrifying bacteria.

Initially the system experiences elevated ammonia levels followed by elevated nitrite levels. Both subside when sufficient populations of nitrifying bacteria are established.

Monitoring ammonia throughout the conditioning process is of questionable value. Little can be done to prevent or compensate for the inevitable rise in ammonia. Even knowing when the ammonia concentration falls to zero is unimportant. This is usually accompanied by high nitrite levels, and it is still unsafe to increase the population of animals until the nitrite concentration is zero, indicating the completion of the initial conditioning.

Nitrite appears shortly after adding animals to a new aquarium, and the maximum is usually encountered in 2 - 4 weeks. The concentration should decrease to zero in 3 - 6 weeks.

Monitoring nitrite during conditioning provides a convenient measurement of progress and will indicate the point at which additional animals can be safely introduced. An approximate position on the nitrite curve can be estimated by comparing measurements on consecutive days. Once the concentration begins to decrease, it is usually only a short time before conditioning is complete.

In aquariums that have not been seeded with a substantial amount of conditioned gravel, nitrite concentrations can exceed 5 mg/l NO₂--N, and a test should be chosen that is capable of measuring the high concentrations that are encountered during conditioning. Tests that have only low range capability are not as useful because they indicate beyond their maximum readable concentration for much of the conditioning period. Of course, it is essential that the test clearly indicate when the nitrite concentration has fallen to zero.

Established Systems

Monitoring ammonia and nitrite in an established aquarium provides information on the condition of the biological filter. Nitrification in the filter is so efficient that ammonia and nitrite should be virtually undetectable.

Presence of ammonia or nitrite indicates that the filter is not capable of handling the biological wastes to which it is subjected. Common causes include:

- (1) Overcrowding.
- (2) Overfeeding.
- (3) Undiscovered dead animals.
- (4) Medications.
- (5) Insufficient circulation.
- (6) Irregular cleaning of filter.

Overcrowding is frequently difficult to diagnose because there is no convenient method of determining the carrying capacity of an aquarium. The maximum acceptable animal load depends on a number of factors, including surface area and depth of the filter bed, particle size of filtrant, and flow rate through the filter. Additionally, the type of animal will also affect the amount that can be safely maintained.

There are numerous "rules of thumb" for the maximum allowable concentration of fish. One author may suggest no more than 3 inches of fish per square foot of filter / surface area. Another may indicate that 2 inches in length of fish per gallon is acceptable. There is much confusion.

On a purely subjective basis, it is safe to say that if an aquarium looks too crowded, it probably is. Frequent fighting and general irritability of the fish are other possible indications.

If elevated ammonia or nitrite levels persist, and you have ruled out the other possible causes, then you may reasonably suspect overcrowding. Removal of some of the animals is necessary to reestablish balance.

Overfeeding and undiscovered dead animals are similar situations. In both cases the decomposing organic matter provides ammonia, which increases the load on the biological filter. If the capacity of the filter is exceeded, elevated ammonia or nitrite levels will be encountered.

In either situation, the offending material must be removed, either by net or by vacuum siphoning. The aquarium should then stabilize quickly.

Care should be taken when feeding to insure that significant amounts of food do not go uneaten. The aquarium should be observed frequently to determine that all animals are alive and healthy. Pay special attention to soft-bodied animals, such as anemones, which can decompose rapidly, and foul the aquarium.

Medications may have adverse effects on the bacteria in the filter bed. If elevated ammonia or nitrite levels are observed shortly after medicating, then the biological filter has probably been damaged.

If possible, the animals should be moved to another holding facility while a substantial water change (50% or more) is conducted. Filtration with activated carbon may also help to remove the medication. Under the best circumstances the bacteria recover quickly and the animals may all be safely re-introduced. In some situations, it may be necessary to increase the population slowly just as in a newly established aquarium.

Refrain from medicating in display aquariums. Such treatments are better performed in "hospital tanks" that are reserved specifically for the purpose of medicating. Conditions of treatment are easier to control and there is no risk to healthy specimens in the display tank.

For optimum performance, any biological filter must receive a constant, substantial flow of oxygenated water. If circulation through the filter bed decreases appreciably, incomplete nitrification can occur and ammonia or nitrite may be detected.

The situation is easily remedied by restoring normal circulation. The most common causes of decreased circulation are:

- (1) Plugged air stones or diffusers in airlift tubes.
- (2) Damaged, blocked or "kinked" air lines.

- (3) Worn out or weak air pumps.
- (4) Worn out motors, impellers or other power filter components.

The problem should be corrected by repair or replacement of the defective item.

An appreciable portion of the filtration capacity of a biological filter may be due to bacteria on the surface of detritus particles. If allowed to accumulate for some time, the removal of this detritus results in an appreciable loss of nitrifying ability, and ammonia or nitrite are detected.

If this occurs, it may be necessary to transfer some of the animals to a separate holding facility-to allow the biological filter to re-equilibrate.

To prevent such occurrences, the filter bed should be cleaned regularly to remove accumulating detritus by lightly vacuuming. Usually this is accomplished during removal of water for regular partial water changes.

Aquarists frequently ask, "What is the maximum exposure level for ammonia and nitrite?" or "How much can the fish tolerate without being seriously affected?"

Many studies have been conducted to determine tolerance levels for various species of fish. Unfortunately, the studies are conducted on fish that are commercially valuable, such as salmon and trout, and the results are not necessarily applicable to the types of fish in marine aquariums. Precise information concerning tolerance limits of ornamental aquarium fish is not available.

Nitrification in the filter should be so efficient that ammonia and nitrite should be undetectable. The tolerance of the fish to ammonia or nitrite is irrelevant. Elevated levels of ammonia or nitrite should alert the aquarist to a potential problem. If the condition exists for more than a day or two, then the problem must be found and corrected.

Nitrate, the end product of nitrification, is the only form of inorganic nitrogen that is detectable in a healthy aquarium. Its concentration increases continuously, unless limited by regular partial water changes.

Since nitrate is relatively non-toxic, water changes are not conducted only for the sake of limiting nitrate. There are additional benefits that, although less obvious, are perhaps more important.

Nitrate accumulation is accompanied by other changes. Buffers are depleted and pH decreases. Dissolved organic materials increase. Phosphate increases. Concentrations of other inorganic ions change. The environment becomes increasingly dissimilar to the natural environment. This contributes the increased stress for the aquarium inhabitants, and ultimately may result in disease or death.

It is in the best interest of the aquarist to control these changes as much as is reasonably possible. We can never hope to duplicate the stability of the sea, but we can limit the inherent instability and inefficiency of the aquarium with a conscientious aquarium maintenance program. Nitrate testing can provide valuable information for this programme.

The rate of increase in the nitrate concentration is a function of the bio-load on the system. Many other changes that occur also tend to be in proportion to the bio-load. Thus, nitrate is a convenient "yardstick" to measure the relative biological age of the water. Maintaining reasonable nitrate levels through periodic partial water changes also helps to control and moderate other changes that are occurring in the water.

A maximum concentration of 20 mg/l $\text{NO}_3\text{-N}$ is recommended. However, in non-critical situations, such as ornamental display aquariums, this level is frequently exceeded without serious consequences. For these applications, maximum concentrations of 20 - 40 mg/l $\text{NO}_3\text{-N}$ are probably acceptable.

Each month, 25% of the old aquarium water should be replaced with fresh salt water, and this is usually sufficient to maintain nitrate at reasonable concentrations. Other activities, such as breeding of fishes or feeding experiments, usually require more control and lower concentration limits. In these situations, nitrate testing is indispensable because monthly water changes may not be sufficient to maintain the desired water quality, and, in the absence of any sophisticated equipment, nitrate level will be the most convenient indicator of the condition of the aquarium water.

In addition to nitrate, the nitrification process also produces acid. This acid depletes buffers and results in steadily decreasing pH, which, if uncorrected, will fall below ideal levels. Monitoring pH allows the aquarist to make corrections before the situation becomes dangerous.

Marine aquariums operate comfortably in a pH range of 8.0 to 8.4 with 8.1 to 8.3 considered ideal. The aquarist should strive to maintain pH near the ideal, and to avoid wide fluctuations.

Occasionally the regular partial water changes are sufficient to restore depleted buffers and control pH fluctuations. However, frequently it is necessary to add more buffer between water changes in order to maintain the desired stability. Sodium bicarbonate is commonly used.

The sodium bicarbonate should be added when the pH approaches the low end of the safe range. At this point, one teaspoon per 25 gallons should raise the pH approximately 0.1 pH unit.

Always dissolve the sodium bicarbonate in a small amount of water before adding it to the aquarium. Make changes gradually; no more than 0.1 pH unit per day. It is always better to make small corrections frequently, rather than large corrections occasionally.

A common misconception holds that use of the proper gravel, such as dolomite or crushed

coral, is sufficient to prevent low pH. In fact, at the normal pH of a marine aquarium, the effect of the gravel is slight. The effect of the gravel becomes significant only when the pH falls below 8.0, beyond the recommended range. The gravel alone will not prevent significant fluctuations in pH; some action on the part of the aquarist is always necessary.

Hospital and Quarantine tanks

A hospital tank is an auxiliary aquarium that is reserved for isolation and treatment of new or sick fish. Typically, it is used for short periods and does not have a functional biological filter.

Without a functional biological filter, ammonia is the first waste product that will accumulate. Since a diseased fish is already in a weakened condition, the ammonia must be controlled to prevent subjecting the fish to additional stress.

Ammonia can be controlled by partial water changes, and monitoring ammonia will indicate when a change is necessary. Depending on the size of the tank and the size of the fish, frequent water changes may be necessary to minimize ammonia toxicity problems. It may even prove difficult to maintain less than 1.0 mg/l ammonia-nitrogen. The ammonia level should be maintained as low as is reasonably possible.

Considering the inherent difficulties with hospital tanks, many aquarists question their necessity. However, medication of established display aquariums should be avoided. The effects on the system are often unpredictable. Additionally, should the aquarist encounter unexplained problems in the future, he will always be uncertain whether residual medications are a contributing factor.

A medication is a toxic substance. Although intended primarily to control parasites, few medications are completely harmless to fish. Obviously, treatment of a disease can be accomplished only with medications that are more toxic to the parasites than to the fish.

Some medications have a wide margin of safety. For others the effective therapeutic concentration is only slightly less than the level that is toxic to fish. In any event, the animals are subjected to a stress that may range from moderate to severe.

Additionally, some medications are harmful to the biological filter, and use in a display aquarium can have serious, long-term consequences as discussed previously.

Healthy fish should not be subjected to the potential hazards of medications. A hospital tank is the means of insuring safe treatment without risk to healthy fish.

All systems

Temperature and salinity should be monitored in all aquariums, whether they are new,

established, or hospital tanks.

Temperatures of 70 to 75°F (21 to 24°C) are ideal. Occasionally, during hot weather, it may be impossible to maintain low temperatures.

At elevated temperatures, the oxygen dissolving capacity of water is less, while the metabolism of the animals is speeded up, and they actually require more oxygen. In effect, the holding capacity of the tank is decreased. In such situations, it may become necessary to lower the population of animals in the aquarium.

Ideal salinities are 27 to 31 parts per thousand, which correspond to specific gravities of approximately 1.020 to 1.023. Once the proper salinity is obtained, occasional replacement of fresh water lost to evaporation will maintain the desired salinity with minimal fluctuations. Water used for partial water changes should be adjusted to the salinity of the aquarium before use. Water in hospital tanks should be adjusted to the salinity of the appropriate display tank.

To increase salinity, add more salt. To decrease salinity, add more fresh water.

For both temperature and salinity, consistency is more important than absolute value. Temperature should not fluctuate by more than 1 or 2°F (1°C) in a 24 hour period. During warm periods, adjust the aquarium heater to a temperature only slightly below the maximum temperature to prevent excessive cooling during the night. Salinity should not fluctuate more than 1.0 part per thousand (0.001 specific gravity units) per week

In Summation

Monitoring of various water chemistry parameters can provide valuable information to the serious marine aquarist.

Routine monitoring of ammonia and nitrite may indicate a developing problem in an established aquarium. Measurements of nitrate and pH helps develop a reasonable timetable for routine maintenance, which is the aquarist's most valuable tool for continually providing a healthy environment within the aquarium.

In newly set-up aquariums, nitrite measurements are an indicator of progress in the conditioning sequence.

Temperature and salinity measurements are aids to maintaining a more stable environment. Other measurements serve useful purposes in special circumstances, but are not routinely employed by most aquarists. For example, phosphate levels may be of interest for intensive algal culture.

In choosing test equipment always remember that the value of the test depends on its accuracy. The accuracy of a test is a function of two factors, the accuracy of the standards and

the reliability of the reagents.

Standards, or comparators, are generally one of three types; colored liquids in sealed tubes, colored plastic films or chips, and printed paper. Liquid and plastic types are usually more reliable because paper types tend to discolor easily. Never store any standard in direct sunlight or it will most certainly fade and become useless.

Reliability of reagents depends on the type of reagent and its stability upon storage. Any reagents that have appreciably discolored should not be used. In general, liquid reagents are more prone to deterioration than dry reagents. Refrigeration will extend the life of liquid reagents.

When in doubt, attempt to analyze a solution of a known concentration, to test for accuracy. If such a solution is not available, at least attempt a duplicate analysis to test for repeatability.

Reasonable care and attention will benefit the aquarist who attempts to utilize the information that can be gained through water analysis

Glossary

ABSORBSION - The taking up of one substance by another, usually of a liquid by a solid, involving weak chemical or physical forces. Water is absorbed by a sponge, but it is weakly held, and may be easily removed by squeezing or drying.

ADSORBSION - The taking up of one substance by another involving strong chemical or physical forces. Methylene blue, a chemical dye, can be adsorbed by activated carbon, and then is extremely difficult to remove from the carbon.

AQUEOUS - Of or pertaining to water.

BIO-LOAD - The sum of the contributions and requirements of all the living organisms in an aquarium.

BUFFER CAPACITY - The ability of a solution to resist changes in pH.

CHLORINITY - The weight, in grams, of the chloride ions (Cl⁻) present. This is often expressed as parts per thousand

COMPLEX - A metal ion surrounded by an organic molecule to which it is tightly bound. The organic molecule insulates the metal ion and reduces its activity in solution.

COMPOUND - A collection of atoms of two or more elements, connected by chemical bonds.

CONDITIONING - The process of establishing a biological filter in the aquarium. Sometimes called run-in.

DENSITY - Weight per unit volume. For example, pounds per cubic foot.

DETRITUS - Loosely packed, insoluble solids that accumulate on the aquarium floor.

DISSOCIATION - The reversible breaking apart or separation of a molecule into two or more parts.

ELECTRON - An elementary particle of an atom that carries a negative electrical charge.

ENZYME - A large molecule that promotes biochemical reactions.

EQUILIBRIUM - A state of balance between opposing forces.

Chemical equilibrium is a condition where two opposing chemical reactions are occurring at the same rate.

HAEMOGLOBIN - An iron-containing pigment that is responsible for oxygen transfer in the blood of many animals.

INORGANIC - Referring to chemical compounds that do not contain carbon.

MILLIGRAMS PER LITER - A unit of concentration measurement in the metric system that denotes weight per volume. A milligram is approximately 1/28,000 of an ounce

NEUTRON - An elementary particle of the atom that is not electrically charged.

NITRIFICATION - The sequence of oxidation, by bacteria, of ammonia to nitrite, and nitrite to nitrate.

NITRIFIERS - Bacteria that are capable of oxidizing ammonia or nitrite.

ORGANIC - Referring to chemical compounds that contain the element carbon.

OSMOSIS Referring to flow or diffusion of substances through a semi-permeable membrane, such as a cell wall.

OXIDATION - Chemical addition of oxygen to a substance, often by a series of reactions. Oxidations may be vigorous (fire) or mild (bacterial oxidation of ammonia).

OZONE - A highly reactive molecule composed of three atoms of oxygen. A molecule of normal atmospheric oxygen is composed of two atoms of oxygen.

PARTS PER MILLION - A unit of concentration measurement that denotes weight per weight in equivalent units. One part per million can mean one gram per million grams or one pound per million pounds or any other unit of weight may be used.

PROTON - An elementary particle of the atom that carries a positive electrical charge.

PROTOZOA - Microscopic animals, many of which consist of only a single cell.

SATURATION - State of being filled to the maximum extent.

SOLUTION - A mixture of two or more substances that is uniform throughout. A sample taken from a solution will have the same composition and properties as every other sample taken from the same solution - regardless of the size of the samples.

SURFACE ACTIVE - Capable of modifying the properties of a liquid at a surface or interface.

Calypso Research Report. APPENDIX A .			
THEORETICALLY PERFECT SYNTHETIC OPEN OCEAN WATER - FORMULA			
To 90 kilograms of distilled or de-ionised water at 20 degreeec C.add:-			
PART ONE			
Common Name	Exact Chemical Formula and Grade	Purity %	Weight (grams)
Sodium chloride	NaCl Analytical	99.96	2,378.0000000
Sodium sulphate	Na2SO4 10H2O Analytical	99.0	896.8100000
Magnesium chloride	MgCl2 6H2O Analytical	98.0	1,078.6500000
Potassium chloride	KCl Analytical	99.8	72.7500000
Sodium bicarbonate	NaHCO3 Analytical	100.0	18.3697500
Potassium bromide	KBr Analytical	99.5	9.7351110
Strontium chloride	SrCl2 6H2O Analytical	98.0	3.1455500
Boric Acid	H3BO3 Analytical	99.5	2.5668000
Sodium fluoride	NaF Analytical	99.0	.3000000
Lithium chloride	LiCl.H2O Analytical	99.0	.1697709
Rubidium chloride	RbCl Laboratory	90.0	.0276666
Potassium iodide	KI Analytical	99.8	.0077333.

Aluminium potassium sulphate	A1K(SO4)2 12H2O Analytical	99.5	•0044271
Manganese chloride	MnC12 4H2O Analytical	98.0	•0007655
	Biotin		•0000112
	Cholic Acid		•0000097
	Vitamin B6		•0000095
	Vitamin B12		•OD00075
	Inositol		•0000001
	Pyridoxine		•OD00001
PART TWO			
To 4 kilograms of distilled or de-ionised water at 20 degrees C.add:-			
Calcium chloride	CaC126H2O Analytical	98.0	221•0165000
Sodium phosphate	Na2HP04 12H2O Analytical	99.0	•0250000
Sodium silicate	Na2Si03 5H2O Analytical	95.0	1•1313666
Sodium molybdate	Na2Mo04 2H2O Laboratory	98.0	•0005750
Sodium selenate	Na2Se04 10H2O Analytical	99.0	•0022750
Sodium metavanadate	NaVO3 Laboratory	98.0	•0005550
Uranyl acetate	Uranyl acetate Analytical	99.0	•0002610
PART THREE*			
* Refer to the following notes prior to adding this part.	To 100 grams of distilled water add:-		
	3 mg. ZnS04 7H2O		
	2 mg. Na2HP04 12H2O		
	4 mg. Na2Mo04 2H2O		
	0.6 mg. NaVO3		
	10 mg.FeCl3 6H2O		
	3 mg.A1K(SO4)2 12H2O		
	2 mg.Na2 HAs04 7H2O		
	0.1 mg.CoCl 6H2O		
	1.0 mg.BaCl2 2H2O		
	1.0 mg.MnC12 4H2O.		
	0.4 mg.CuS04 5H2O.		
	1.0 microgram.K2Cr2O7		
(All of the above should be of analytical or an equivalent grade of purity			
Note: Initial precipitation will occur with both parts two and three. These will rapidly redissolve when these parts are added to part one			

Calypso Research Report. APPENDIX A continued

When all three parts of the formula are dissolved, part two should be added to part one, followed by part three being added to these two when mixed.

The quantity of the solution called here part three can be adjusted according to final requirement:-

- (1) If 'Open Oceanic' or 'Tropical Reef' water is desired add 50% of the part three stock solution.
- (2) If Temperate Coastal water is required add all of part three.
- (3) If an intensified culture medium is required the quantities of salts listed in part three may be doubled, & the following salts also added:- (to the final solution)

Magnesium nitrate. $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 0.25 grams

Potassium nitrite. KNO_2 0.015 grams

Ammonium chloride. NH_4Cl . 0.015 grams

Ferric citrate. $\text{C}_6\text{H}_5\text{O}_7\text{Fe}_3\text{H}_2\text{O}$ 0.015 grams

The final solution should be vigorously aerated for a minimum of one hour prior to use. then corrected to 1.025 S.G. it will yield a solution conforming to the requirements of the the text tables. It will also show the following characteristics:-

pH 8.2 +0.1

Salinity 35 ‰ S.

Chlorinity 19 ‰ Cl.