An Innovative Student Project to Develop a Precision Instrument for Undersea pH Measurements

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Abstract

The present paper describes the design and prototype construction of a teleoperated robotic sensor for precision pH measurement of sea water at deep ocean locations. The need for such an automated device originated with NOAA. The design and construction was undertaken at the USF Mechanical Engineering Department's Robotic Systems Laboratory. The completed prototype will be utilized for research purposes by the USF Marine Science Center in St. Petersburg.

Introduction

The design work centered around the automation and miniaturization of an existing laboratory procedure to facilitate remote undersea precision pH measurement (to 1/1000th of a pH unit). The laboratory procedure known as spectrophotometric testing [1] involves 6 basic steps:

1. **sample the sea water or fill** - collect sample at the appropriate depth.
2. **base-line test** - spectrophotometrically analyze a controlled light source passing through the sample.
3. **indicator-dye injection** - injecting a metered amount of indicator-dye into the sample.
4. **indicator-dye mix** - mixing the dye into the sample.
5. **dye-reacted test** - spectrophotometrically analyze a controlled light source passing through the sample.
6. **test chamber flush** - thoroughly eject current sample to allow recycle to next sample.

The layout of the device involved subdividing the 6 basic steps into three groups, each containing 2 steps; namely: **fill/flush, base-line test/dye-reacted test,** and **dye injection/dye mix.** The 3 groups were accommodated with a revolving cylindrical core placed within an outer casing. The core contained a test chamber which served as a container for the sample and would revolve on a central shaft supported by bearings. Each of the 3 groups of operational steps were given a station position, such that the test chamber was able to be indexed to each station in turn where the appropriate procedures could be performed.

Constraints & Material Selection

The constraints on the design fell into 2 major categories: *material & operational*. The material constraint is that neither the sea water sample or indicator dye could make any contact with metals as this would adversely affect the precision of the pH measurement. The operational constraints were that the device must maintain proper function in any physical orientation and the sample could not contain air pockets.

The former operational constraint arose from the fact that specific orientation of the towed instrument platform into which the device was to be fitted could not be assured. This constraint's main impact on design was that gravity could not be utilized to ensure successful operation. For example, any valves, linkages, or solenoids would require spring or magnetic returns.

Air pockets had to be avoided during spectrophotometric testing since these would interfere with the controlled light source beamed through the sample.

The material constraint meant that the major components of the device would need to be non-metallic. Ceramics were not used due to machining limitations. This left a vast array of plastics to be examined. The choice of plastic materials was narrowed because of the need to avoid those that readily absorb water, such as Nylon. If the core material was made from absorbent plastic, traces of old sea water samples and dye could cause a cross contamination problem. Property comparisons of common plastics showed that fluoroplastics such as Teflon (DuPont) had the lowest water absorption. Another low water absorption plastic found was Noryl (GE Plastics). The actual water absorption for each based on ASTM test D570 were: Nylon, 2.3%; Teflon (polytetrafluoroethylene or PTFE), <0.01%; and Noryl (polyphenylene ether), 0.07%.

PTFE seemed ideal in terms of absorption, but its tendency to deform under a load (cold flow or creep) is poor. In order to reduce creep in PTFE, glass fibers can be incorporated into it. This "filled" PTFE posed the problem of exposing and dislodging of surface glass fibers during machining, leaving a dimpled surface within the test chamber. This would reduce its ability to completely shed the sea water sample. A non-filled PTFE derivative called Hostaflon (Hoechst AG) is an advanced chemically modified version of PTFE which exhibits a much lower creep rate.

Since the core is essentially the test chamber and only moderately loaded, Hostaflon with its low water absorption and improved strength, was chosen.

The case would involve passages for the sea water and therefore could not be metallic. This case would also provide mounting points for the sub-systems and provide the structure for the device and needed to be fairly rigid. The choice was made to use Noryl. The water absorption criteria was important but less of an issue for the case due to minimized sea water contact.

Design Details and Construction

The details of the final design can be described by reviewing each component and each of the 3 stations. The following sections expound the details of the design and where appropriate, the methods of actual construction are discussed.

Core: The core was essentially a cylindrical piece of Hostaflon 4" Long x 3" Diameter. This part only needed a few holes bored through it for the test chamber (20mm dia.) and center indexing shaft. Although only one hole is required for the test chamber, 2 additional identical holes or dummy chambers were placed in the core. The two dummy chambers allowed sea water to continuously flow through the core when the test chamber was away from the flush/fill station. This continuous flow

through the device ensured that samples would always be current and appropriate to the platform's position, rather than "old" water trapped in the inlet plumbing.

The center indexing shaft needed to be firmly keyed into the core's relatively soft material to prevent slippage. If it were to slip, the external indexing system would not be able to line the test chamber up to the stations properly. A non-round cross-section shaft was chosen as traditional keys or pins would easily strip-out. Either a triangular or hexagonal shaft would have made good choices given the symmetrical geometry of the 3 chambers in the core. The triangular shaft was abandoned as finding such shaft stock and making a triangular hole in the core would prove difficult. Conversely, placing a hex hole into the core was easily done with a standard hex broach (3/8" across flats), and stainless-steel hex bar stock was readily available.

The only other machining processes required by the core were to cut grooves around the chambers for the o-rings. These were simple square channels that were cut using a trepanning tool to a depth which would allow the o-rings to compress properly.

Outer Case: The outer case consisted of 3 components: the case and 2 end caps. The case is simply a hollowed out section of the 4 inch diameter Noryl rod used to separate the end caps and enclose the core. The Noryl end caps, which were 2 inches thick, contained all external details for the 3 stations. Each station was unique, but the fill/flush and base-line/dye reacted test stations were identical on both end caps. The case and end caps are clamped together using six 1/4 inch threaded rods equally spaced at 60 deg. intervals around the perimeter. The interface between the case and end caps is sealed using a 0.020 inch thick PTFE gasket. The overall assembled length of the case and end caps is approximately 8 inches.

The inlet and outlet ports for the flush/fill station were plumbed into the caps to permit sea water entry from the sides thereby leaving the ends free for other attachments. The ports were slotted to prevent any large debris from entering the test chamber and to keep the chamber o-rings seals in position as they slid across the opening while indexing. This slotted strainer was accessible for clean out from the ends of the caps by removing a transparent threaded plug.

The base-line/dye reacted testing station featured glass windows flush mounted into the core side of the end caps. These windows were secured in place with a snug fit and RTV silicone. Fiber optic fittings were placed immediately above the windows and secured in place by their threads. This required that the end caps be thinner at this station than the nominal 2 inch thickness at the others. The thinning was accomplished by plunging a milling cutter into the side of the end cap to create a U-shaped cove into which the fitting was placed. This also guaranteed a gentle bend radius for the fiber optic cables.

The dye inject/mix station features an injector nozzle and an external mixing magnet access. This is the only station where the 2 end caps are not identical. The external mixing magnet access was simply a blind hole which centered over the test chamber. This blind hole has a very thin bottom to allow the magnetic force to reach into the test chamber and engage the integral magnetic head. The dye inject end cap required a stepped hole to allow the injector nozzle to be flush mounted on the core side of the cap, while the external side of the cap was threaded to accept the small bore tubing

fittings which came from the dye injection pump.

Core Indexing: The task of core indexing would be accomplished with a D.C. electric motor directed through a driving mechanism attached to the core's central hex shaft. The indexing rotates the core from station to station in 120 deg. increments within the case. Specifically, the rotary motion of the core is **from** *the fill station* **to the** *base-line test station* **to the** *dye injection/dye mix station* **reversing back to the** *dye-reacted test station* and **finally to the** *flush station*. Note that there are 3 stations providing 2 procedures each depending upon which direction the core is moving. The driving mechanism needed to provide for accurate and repeatable positioning, reversibility, reasonably quick reaction to inputs from the motor, and locking at any particular station.

A Geneva mechanism was used between the motor and shaft. This mechanism differs from gearing in that it provides repeatable, intermittent rotary output for a constant input. In fact, this intermittent rotary output is provided through discrete, accurate swept angles and is not affected by backlash. The Geneva mechanism also provided for locking and dwell at the locked positions. The dwell allows the output of the mechanism to remain stationary as the input coasts down after the motor is switched off. The Geneva mechanism was ideal for the task of core indexing.

The core shaft was constructed of stainless steel hex stock since no sample contact is involved. One end was machined to fit in a plastic radial ball bearing placed within a blind hole in one end cap. This ball bearing consists of glass balls with acetyl races and is completely non-corrosive. The other end of the shaft was machined to a 0.25 inch round section that protrudes through an end cap and connects to the Geneva mechanism and a position encoder using a 1/16 of an inch square key. The round section was provided with 2 grooves for quad-lobed o-rings which prevented sea water escaping beyond the case. The round area just beyond the double quad-lobed o-ring seals provided a bearing surface for this end of the shaft. The bearing used was a plain PTFE type.

The shaft's hex section is 10 cm long and fits entirely within the core providing the keying action needed to prevent the core from slipping with respect to the shaft.

Fill/Flush: The filling and flushing station's sole purpose is to gather a sea water sample in the test chamber and eject this sample once the testing has been completed. This task required that the sample have no air pockets in the test chamber. As a result, design attention was focused on sealing the cylindrical test chamber's ends effectively to prevent leaking. Gathering the sample would be accomplished by simply rotating the test chamber away from the constant flow of sea water quickly to capture a "slug" of water. This assumes that no air bubbles are in the incoming sea water and that several initial purging cycles will be required at start-up. Flushing occurs when the test chamber is returned to the station and the flow of sea water removes the tested sample.

The fill/flush station consists of inlet and outlet ports in the case's end caps. These ports provide a path for the sea water to enter and exit the device. The ports were designed with common non-metallic tube fittings for simplicity. The ports also incorporated a straining mechanism (see previous section) to prevent any large debris from entering the test chamber.

The test chamber seals were important in keeping the sea water sample contained. The first choice

in circular seals are o-rings, since they are widely available. The usual application for o-rings is for seals on a rotating or sliding shaft. This application called for sealing to occur between 2 flat faced surfaces. The motion between the surfaces would also be a sliding motion. For o-rings to reliably make a seal, they must be compressed to a certain degree. A common rubber o-ring would have produced such a large frictional force that indexing the core would have required large amounts of torque to accomplish. The frictional characteristics of the o-rings had to be reduced.

Low friction solid PTFE o-rings exist but these require high forces to seal reliably. More research found PTFE coated rubber type o-rings. These are simply ordinary o-rings to which a very thin layer of PTFE has been deposited. Unfortunately this coating wears away very quickly such that the o-rings would need frequent replacement. Finally, it was discovered that PTFE encapsulated o-rings were available. These are essentially o-rings made of thick-walled PTFE tubing into which a rubber compound has been injected. These act much more like an ordinary o-ring than a solid PTFE o-ring in that they seal with lower forces because they easily compress. They also have the improved frictional characteristics needed due to the PTFE.

Dye Injection: The spectrophotometric testing required that an indicator dye be injected into the sea water sample. A dye volume of 20 µl was specified based upon the volume of the 2 cm diameter by 10 cm long cylindrical test chamber. This small volume of dye needed to be precisely delivered to the sample in order for accurate results to be obtained. Additionally, the dye could not encounter any metallic components.

The injection of these small amounts of dye was handled using a micro metering or dispensing pump. The model chosen is a positive displacement adjustable metering pump with a dispensing range from 0 - 50 µl per pump revolution. The pump head on this model is completely non-metallic and is powered by a stepper motor which allows complete control and accuracy for each dispense. The pump head included special small bore tubing fittings for routing the pump's inlet and discharge.

The pump's discharge would be plumbed directly into the test chamber, but there is a finite volume of dye involved in the tubing between the pump and the test chamber. Therefore a potential problem existed of "leaching" the dead volume of dye from within the tubing during mixing and destroying the accuracy of the dispense. A positive closing off of the tubing directly at the point where it entered the test chamber was needed to prevent this problem. A check valve was needed at this location. This check valve would need to be non-metallic and relatively small. The final valve utilized a silicone rubber diaphragm held in position with spiral arms which act as springs to keep the flow shut off if there is no pressure pushing on the diaphragm. The result is that the flow will only occur in one direction. These commercially available valves were designed to be placed in-line with tubing, and had to be substantially modified to work as a flush mount directly over the test chamber at the dye injection station, therefore acting as a dye injector nozzle.

The dye injects into the test chamber which does not contain any air pockets. This poses a problem: how is the dye going to fit into a completely filled space? The required extra volume was accommodated by simply including an air-filled ring inside of the test chamber made of hollow rubber tubing. This ring would compress the slight amount required when the pump injected the dye under pressure. This hollow ring did not interfere with the function of the device since it was ring

shaped and allowed the light to shine through its center. When the test chamber returns to the flushing station, the pressure from adding the dye is released and the tubing restores to its original shape.

Dye Mix: The purpose of the dye mixing station was to thoroughly distribute the indicator dye into the sample. The fact that the sample has no voids or air pockets means that there is no free surface within the test chamber. This greatly hampers normal mixing such as shaking methods. The lack of a free surface (within the sample) dictated that mixing would need to be facilitated by a physical stirrer of some sort inserted into the test chamber. The final design employed a magnetically coupled stirrer.

The stirrer would consist of a plastic head into which magnets would be incorporated, attached to a lower mixing element. The stirrer would then be magnetically coupled to a rotating external magnet. The internal magnet would consist of small, very strong thin round magnets arranged in a plastic housing to act as a horseshoe magnet. The strength of these rare earth or neodymium iron boron magnets is impressive (0.5 lb.) for their size: 0.187 inch diameter by 0.060 thick. The magnets are arranged in stacks of 3, which provides a length to diameter ratio near 1 (0.180/0.187) for maximum magnetic force per mass of magnet. The 3 stacks per pole/side or 6 stacks total are backed by a thin steel washer for a return magnetic path. The external magnet would take the form of a cylindrical horseshoe magnet with a hole through its center. The external magnet would be driven around using a D.C. electric motor connected to a shaft passing through the center of the magnet.

The mixing element chosen had a helical shape since this would act as a miniature pump and readily provide a mixing current within the test chamber. The configuration would also allow a small amount of compression, forcing the magnetic coupling head to always remain in the vicinity of the external magnet so drive would be assured regardless of orientation. The open center of the helix allowed unobstructed passage of the light beam.

The next and final step in the evolution of the dye mixing system was construction of a non-metallic helix. Plastic coil springs are not readily available commercially, so one would need to be made in house. The basic technique is to cut a large acme screw thread into a thick walled plastic tube using a lathe.

Spectrophotometric Test: The actual measurement of pH occurs here at the base-line and dye-reacted test station. Spectrophotometric testing uses an indicator dye which reacts to the sample's pH and changes its spectral absorption. This change is measured against a non-reacted spectral absorption measurement called the base-line test.

The spectrophotometric testing involves shining a controlled light source through the test chamber. This light is generated by a separate specialized device, which also collects the light and analyzes it. The light is transported to the pH measuring device via fiber optic cables with focusing end fittings. These fittings had stainless steel bodies and so could not come into contact with the sample. The fittings, which were mounted into the end caps with threads, were placed behind circular glass windows fitted flush into the end caps to provide an uninterrupted surface for the o-rings to glide past. The fiber optic fittings had to be rigidly fixed to ensure their alignment. The fiber optic

cables had to be routed with generous bend radii to ensure the required optical quality.

Conclusions

The device was designed and constructed to reproduce an existing laboratory process. The device does indeed function and closely mimics this laboratory procedure. Testing beyond the functional stage will be performed by placing it on a towed submersible instrument platform currently under development.

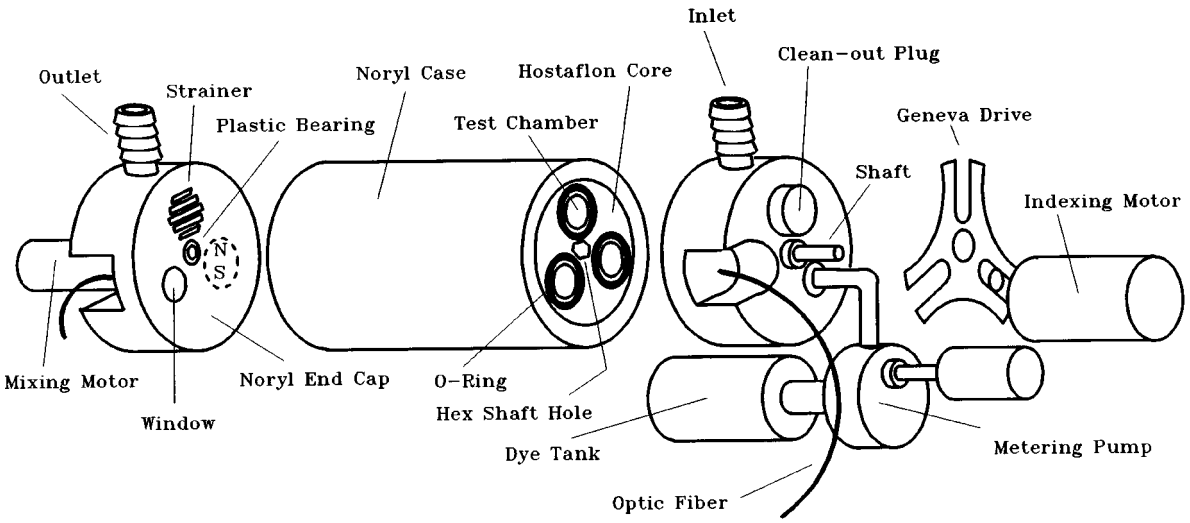

Figure 1. - Exploded View of pH Measuring Device (internal Helical Mixer not shown)

Reference

[1] Byrne, R.H. & Clayton, T.D., "Spectrophotometric sea water pH measurements: total hydrogen ion concentration scale calibration of m-cresol purple and at-sea results." Deep-Sea Research I 40, no. 10 (1993): 2115-2129.

Biographical Information

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