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INCREASED SENSITIVITY IN MEASUREMENT OF BUTYLTINS IN SEAWATER
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INCREASED SENSITIVITY IN MEASUREMENT
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Increasing controversy over the use of tributyltin based antifouling paints and its impact on the marine environment has made the development of techniques to measure part per trillion (ng/L) levels necessary. Modifications of the method developed by Hodge, et. al. [1] and the Naval Ocean Systems Center [2,3] have increased the sensitivity by a factor of ten, from 4 ng/L to 0.4 ng/L for (n-Bu)₃ Sn. It is evident from work by Donard, et. al. [4] that the design of the quartz burner can influence sensitivity. A closed end quartz furnace was found to give optimum sensitivity in our work.

The optimized system consists of a modified 500 ml gas washing bottle (hydride generator) with an outlet on the top and an injection port on the side. Teflon tape is wrapped around 1/8 inch O.D. teflon tubing to form a secure seal when the tubing is threaded through the top outlet. This tubing is then pressure fit into the end of a 3mm I. D. glass U tube (2 1/2-3 inch sides) which forms the cryogenic trap for the tin hydrides. Avoiding the use of Swagelok fittings improves the analysis. It is important that the glass traps be thoroughly clean and the active sites which complex the hydrides and cause peak reduction or broadening be sealed. The traps are cleaned by soaking in hot 20% Pierce RBS 35 in distilled water rinsed and dried. The traps are washed with hexane and methanol and dried in a 110° oven. While still warm they are filled with silanizing fluid (Supelco Silon CT) and allowed to sit for thirty minutes. The traps are then thoroughly flushed with hexane and methanol and dried in a 200° oven for 10 minutes. Twenty to thirty milligrams of 3% OV-1 on 80/100 chromsorb W HP are added and secured with silanized glass wool plugs.

The trap is connected to the quartz burner with another teflon tube fitted with a glass capillary tip. The tip is positioned at the edge of the barrel of the burner and the tubing secured by a Swagelok reduction fitting.

Samples are analyzed by hydride derivatization and hydrogen flame atomic absorption spectroscopy using parameters previously described [3]. The quartz burner design concentrates the evolved tin

hydrides in a small area resulting in an intensified signal. All lines and the trap were periodically flushed with dry helium to remove water vapor. This is important to retain sensitivity and increase the life of the trap. The traps must be thoroughly dried with helium purging between runs. Figure 2 shows typical results of the analysis of a seawater sample with fairly low butyltin concentrations. The absolute detection limits were obtained by running a series of blank seawater samples spiked with 0.5 ng each of mono, di, and tri-butyltin chloride. The detection limits based on 3σ of these near background standard additions are 180 pg tributyltin, 80 pg dibutyltin and 120 pg monobutyltin calculated as the cation.

References

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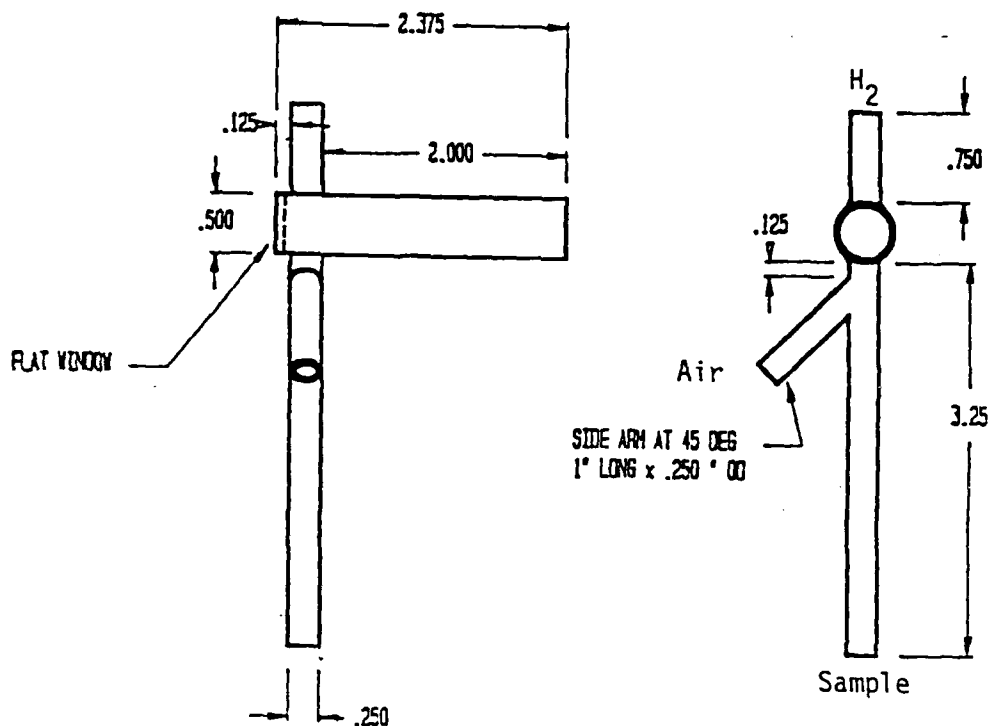


FIGURE 1. CLOSED END QUARTZ BURNER (DIMENSIONS IN INCHES)

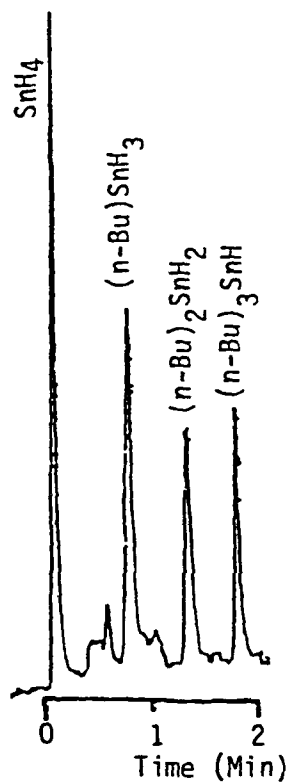


FIGURE 2. SPECIATION OF BUTYLTINS IN SEAWATER. AMOUNT OF COMPOUNDS AS THE CATION IS AS FOLLOWS $(n-Bu)Sn^{+3}$ 1.3ng
 $(n-Bu)_2Sn^{+2}$.64ng $(n-Bu)_3Sn^{+}$ 1.3ng