An Acoustic Wave Sensor for Monitoring Ammonium in Water

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The rearing and maintenance of finfish and shellfish in aquaculture is important in both industry and research settings. Careful regulation of either freshwater or marine environments is critical for optimal growth and disease resistance of the organisms in culture. An important waste product that may accumulate in closed aquaculture systems is ammonia. The presence of ammonia is indicative of suboptimal water treatment or other imbalance of the aquaculture system. Ammonia toxicity in aquaculture systems typically becomes problematic at concentrations between 0.005 and 0.05 mM (mMole/l). Colorimetric chemical methods and ammonia-specific electrodes are currently used for monitoring ammonia levels, but these methods are expensive, slow and cumbersome to perform, or suffer from problems of drift and poor longevity. Development of a robust, easy to use and inexpensive ammonia/ammonium sensor will permit more frequent monitoring of water quality in aquaculture systems and reduce their operating costs. In the present study, a novel quartz crystal microbalance (QCM) sensor, which is capable of on-line ammonium monitoring has been developed.

The sensor used in this study was a 5 MHz thickness shear mode (TSM) AT-cut quartz resonator with a novel electrode configuration, which is shown in Fig.1 (b). Compared with the standard QCM sensor (Fig.1 (a)), the sensing electrode of the new device is much smaller than the reference electrode, which allows significant penetration of the electric field associated with the TSM into the liquid. This allows one to measure the changes in the conductivity and permitivity of the liquid caused by the target analyte of interest. In aqueous solutions NH_3 and NH_4^+ exist in an equilibrium state that is controlled by pH. Since the highest level of QCM sensitivity is achieved in the detection of the ionized species, preliminary tests were performed with solutions of the salt, ammonium acetate. A commercial oscillator was used to drive the sensor operating in the fresh aquaria water. Small volumes of 1 M ammonium acetate were injected into 68.2 ml water and the frequency output was measured.

Fig.2 shows the frequency response of the sensor in the experiment. It can be seen the resonant frequency of the sensor drops each time the ammonium acetate is injected. The frequency shift as a function of ammonium concentration is shown in Fig.3 along with that of the standard QCM sensor. The fresh aquarium water is used as a reference. Since the conventional QCM is not sensitive to the liquid electrical property changes, the slight increases in QCM frequency is due to the change of the liquid mechanical loading (density viscosity product). However, the frequency of the new QCM device is influenced both by the liquid electrical and mechanical property changes. It decreases significantly in the low concentration range due to the electrical property changes caused by the ammonium acetate, and then the curve begins to flatten due to the larger influence from the liquid mechanical property changes.

In conclusion, it is shown that a novel QCM sensor can detect ammonium in water in the concentration range where the ammonia toxicity in aquaculture systems becomes problematic.

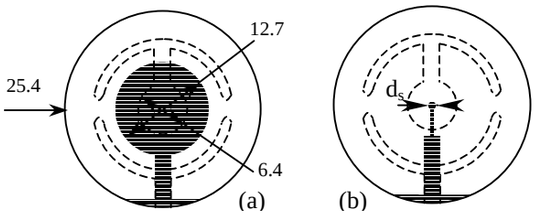

Fig.1 Geometry of (a) the standard QCM sensor and (b) the QCM sensor with the small electrode configuration, where d_s=0.8 mm. The dark area represents the sensing electrode in contact with the liquid.

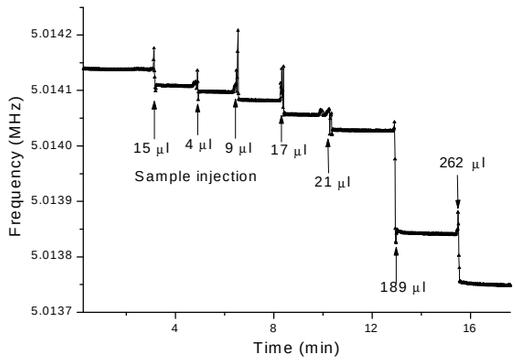

Fig.2 The frequency response of the new QCM sensor as the ammonium acetate was injected into the aquaculture system water. The spikes in the frequency response at the beginning are due to the injection operation.

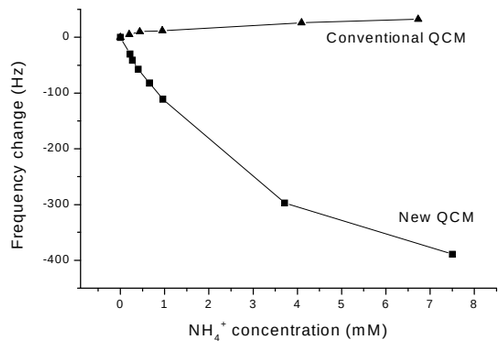

Fig.3 Frequency shift of QCM sensors as a function of ammonium concentration in the aquaculture system water.