

# **Report as of FY2006 for 2005KS40B: "A Real-Time Permittivity Sensor for Simultaneous Measurement of Multiple Water-Quality Parameters"**

## **Publications**

Conference Proceedings:

o KSU filed a provisional patent application for “Frequency-response sensors and associated signal conditioning/processing for real-time and simultaneous measurement of properties of dielectric materials” in the US patent Office (Docket No. 37057-PRO) on March 8, 2006.

## **Report Follows**

**Project Title:**

A Real-time Permittivity Sensor for Simultaneous Measurement of Multiple Water-Quality Parameters

**Start Date:** March 1, 2006

**End Date:** February 28, 2007

**Investigators and Affiliations:**

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**Keywords:** Sensor, Water Quality, Water Contaminants, Nutrient, Pesticide.

## Problem and Research Objectives

This is the second year of the project. The main objective of the research work is to develop a novel, frequency-response permittivity sensor to measure multiple properties of surface and ground water that are crucial to water quality.

## Methodology

### 1. Sensor improvement

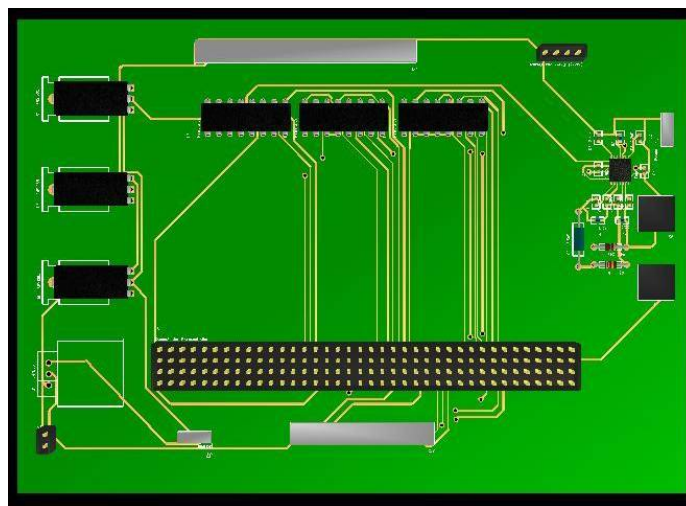
Considering the effect of corrosion on measurement, we made two new sensors using aluminum alloy and stainless steel (Figure 1). Geometry of the sensor probe was modified to further enhance the capacitive effect. Sealing of the probe was also improved to achieve complete waterproof.



**Figure 1. Sensor probes made of (a) aluminum alloy and (b) stainless steel**

### 2. Hardware design

A printed circuit board (Figure) was designed and fabricated. User interface with a keypad and a LCD screen was also designed. The hardware was integrated into a portable box (Figure 3), which was designed for field tests.



**Figure 2. Printed Circuit Board for signal processing**



**Figure 3. Signal conditioning/processing and user interface**

### **Significant Findings**

Four water tests were conducted for the sensor. Findings from the tests are reported below.

#### *1. Test in three separate Potassium solutions*

A modified sensor probe (Figure 1) was tested in water solutions of three potassium salts,  $\text{KNO}_3$ ,  $\text{KH}_2\text{PO}_4$ , and  $\text{KCl}$ . The experiment was conducted in two steps. During the first step, we tested the solutions in high salt concentrations (3,500 – 35,000 ppm). The goal was to identify FR signatures of individual cation and anions. For each salt, 11 solution samples with increasing concentration were prepared in deionized water. Frequency-response data were then taken three times using the sensor. Calibration models for predicting the salt concentrations were established for individual salts. Results are shown in Table 1.

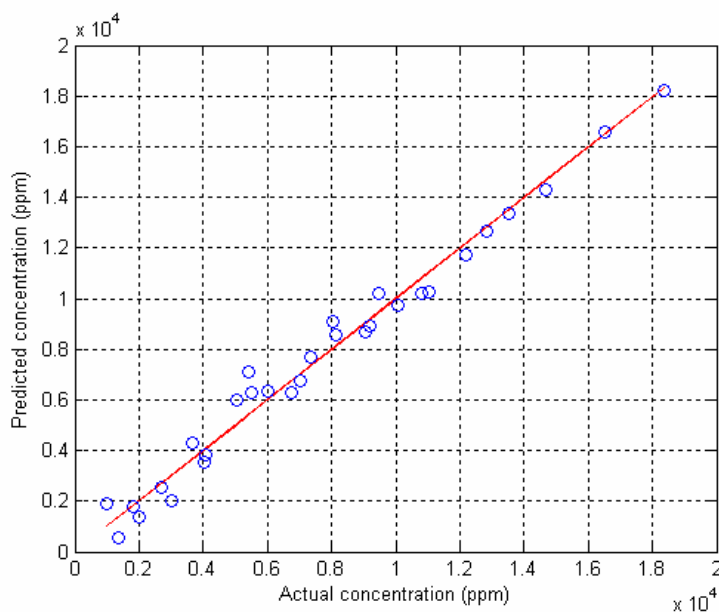
**Table 1. Prediction results for three salt solutions at high concentrations  
(3,500 – 35,000 ppm)**

Salt type	R-square value	RMS error (ppm)
$\text{KH}_2\text{PO}_4$	0.9985	390
$\text{KNO}_3$	0.9848	1273
$\text{KCl}$	0.9927	857

In order to test the sensor's ability to recognize specific ions in water solutions, FR data for all three salts were combined to establish PLS models to quantitatively predict individual ions. The results are shown in Table 2. The prediction results for potassium ion across three salt types are shown in Figure 4.

**Table 2. Prediction results for ions and cation in three salt solutions at high concentrations (3,500 – 35,000 ppm)**

Anion/Cation	R-square	RMS error (ppm)
K <sup>+</sup>	0.9801	640
Cl <sup>-</sup>	0.9532	1109
NO <sub>3</sub> <sup>-</sup>	0.9649	1238
PO <sub>4</sub> <sup>-</sup>	0.8323	3078



**Figure 4. Prediction result for potassium ion concentration in three high-concentration salt solutions**

The second step of the experiment was to test salt solutions at low concentrations (0-4 ppm). The salt tested was potassium nitrate. Samples of 11 concentrations were prepared using a dilution procedure. Three independent sets of samples were prepared. One set was used for calibration; the others for validation. The results are shown in Table 3. These results prove that the sensitivity of the sensor is sufficient for measuring nutrient residual in water at the environmentally- and physiologically-relevant concentration level.

**Table 3. Prediction results for K<sup>+</sup> in three salt solutions at low concentrations (0-4 ppm)**

Data set	R-square	RMS error (ppm)
Training data set	0.9988	0.041
Validation data set 1	0.9217	0.775
Validation data set 2	0.8710	1.408

Frequency signature

Conventional multivariate analysis tools, such as partial least square (PLS) method, have been proven effective in spectroscopic data analysis. In order to reduce the number of frequencies used in the model, “signature frequencies” for a specific agent, at which the frequency response of the agent possesses distinguishable patterns from other agents, should be selected. One way to select the signature frequencies is to locate the peaks (both positive and negative) in the loading factors (principal components) derived from the PLS analysis for that specific agent.

From the first three principal components (PC) derived from the PLS analysis on potassium cation (K<sup>+</sup>) using 33 solution samples of KCl, KNO<sub>3</sub>, and KH<sub>2</sub>PO<sub>4</sub> (11 samples for each), 30 signature frequencies were selected from 606 frequencies originally used in the FR data. PLS models established using the 30 signature frequencies were tested in samples of individual and combined salt solutions to predict the concentrations of potassium cation (K<sup>+</sup>). As shown in Table 4, the 30 signature frequencies did a very good job in detecting the cation concentration with high R<sup>2</sup> values and low RMS errors, especially for the KCl and KH<sub>2</sub>PO<sub>4</sub> solutions. This result indicates that, once correctly identified, the signature frequencies can be used to detect specific ions in water samples with unknown pollutants. The reduced number of frequencies would not only speed up the measurement, it would also avoid overfitting of the prediction models.

**Table 4. Prediction results for K<sup>+</sup> in different salt solutions using a PLS model established based on 30 “signature frequencies”**

Solutions tested	Number of samples tested	R <sup>2</sup>	RMS error (ppm)
KCl	11	0.9909	503
KNO <sub>3</sub>	11	0.8084	4401
KH <sub>2</sub> PO <sub>4</sub>	11	0.9999	25
KCl, KNO <sub>3</sub> , and KH <sub>2</sub> PO <sub>4</sub>	33	0.9071	1383

When the 30 signature frequencies obtained using high-concentration solutions were used to predict low-concentration (0-4 ppm) KNO<sub>3</sub> solutions, the R<sup>2</sup> value for the training data set was basically unchanged. For validation, the R<sup>2</sup> value slightly decreased for data set 2 but increased for data set 3 (Table 5). The difference between these two was greatly reduced. This demonstrates the effectiveness of the frequency signature in describing the FR patterns of specific types of ions and in avoiding model overfitting.

**Table 5. Effectiveness of frequency signature in reducing the number of frequencies while achieving better prediction for low concentration (0-4ppm) KNO<sub>3</sub>.**

Data set	Data set 1 (Training)		Data set 2 (Validation)		Data set 3 (Validation)	
Frequencies used	606 (original)	30 (Signature)	606 (original)	30 (Signature)	606 (original)	30 (signature)
R <sup>2</sup> values	0.9991	0.9992	0.9560	0.9153	0.8207	0.9140

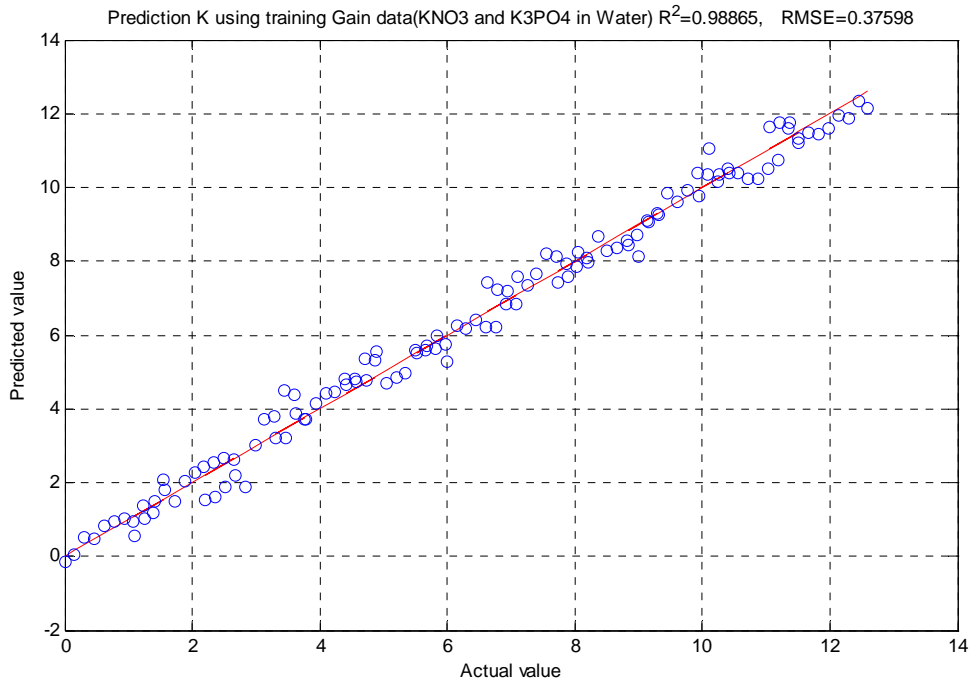
2. Detecting potassium ion in mixed salt solutions

Two sets of 121 mixed Potassium Phosphate (K<sub>3</sub>PO<sub>4</sub>) and Potassium Nitrate (KNO<sub>3</sub>) solutions were prepared by blending 11 Potassium Phosphate solutions (0-20ppm) with 11 Potassium Nitrate solutions (0-4 ppm). One set was used for training and the other validation. Models were established to predict the concentration of potassium ions in the mixed solutions. The results are list in table 6. Figures 5 and 6 demonstrate the prediction results for potassium ion for the training and validation data sets, respectively.

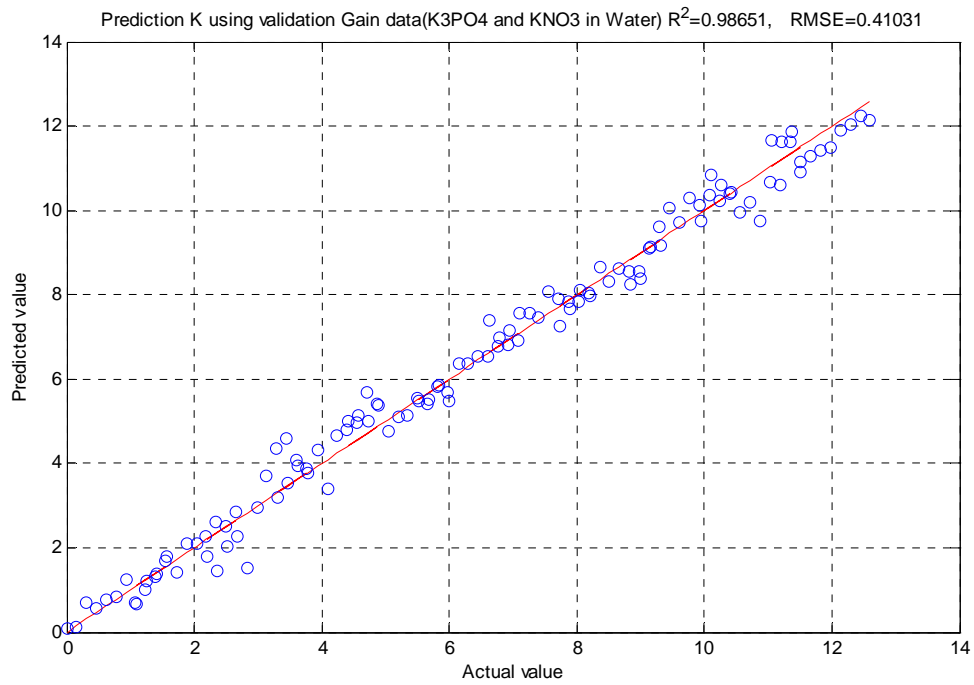
It can be noted from Table 6 that, when 30 “signature frequencies” were used, high prediction accuracy was maintained.

**Table 6. Predicting potassium ion concentration in mixed salt solutions**

	Data type	R-square	RMS error (ppm)
Training	Gain	0.9887	0.376
	Gain (30 “signature frequencies”)	0.9708	0.603
	Phase	0.9878	0.390
	Gain and phase	0.9885	0.379
Validation	Gain	0.9886	0.410
	Gain (30 “signature frequencies”)	0.9645	0.679
	Phase	0.9880	0.430
	Gain and phase	0.9878	0.436



**Figure 5. Prediction K<sup>+</sup> using training gain data**



**Figure 6 Prediction K<sup>+</sup> using validation gain data**

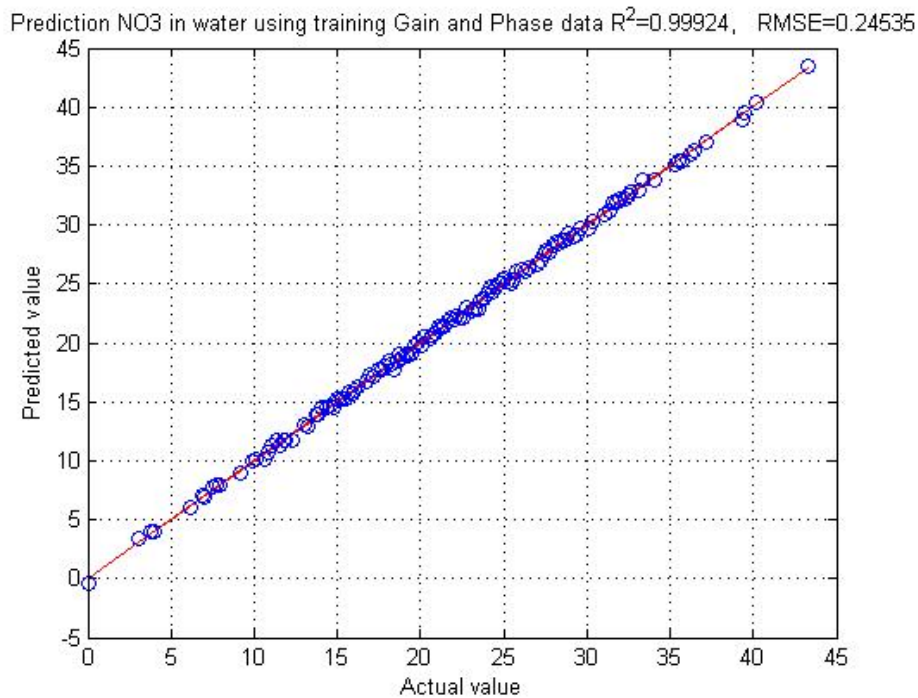


3. Simultaneously detecting nitrate and three salts in mixed salt solutions

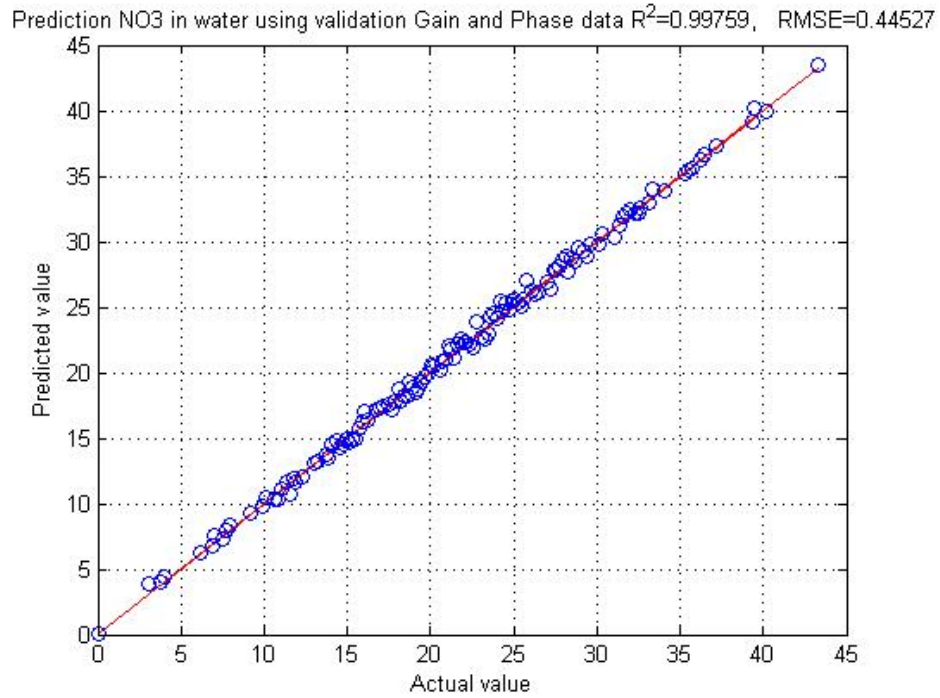
Two sets of 125 mixed salt solutions were prepared. These included combinations of five Potassium Nitrate ( $KNO_3$ ) concentrations, five Calcium Nitrate( $Ca(NO_3)_2$ ) concentrations, and five Ammonium Nitrate( $NH_4NO_3$ ) concentrations. The five concentrations were 0, 5, 10, 15, and 20 ppm. One set of the 125 mixed solutions were used as the training data set, where as the other for validation. The goal was to predict the nitrate concentration, as well as concentrations of Potassium Nitrate, Calcium Nitrate, and Ammonium Nitrate, simultaneously, in all samples. The results are shown in Tables 7 through 10. Figure 8 shows the prediction using both gain and phase training data.

**Table 7. Predicting Nitrate concentration in blends of three salt solutions**

Data set		R-square	RMSE (ppm)
Training	Gain	0.9987	0.320
	Phase	0.9990	0.284
	Gain+Phase	0.9992	0.245
Validation	Gain	0.9973	0.481
	Phase	0.9971	0.484
	Gain+Phase	0.9976	0.445



**Figure 7. Prediction result using both gain and phase data for the training data set**



**Figure 8. Prediction result using both gain and phase data for the validation data set**

**Table 8. Predicting Potassium Nitrate concentration in blends of three salt solutions**

Data set		R-square	RMSE (ppm)
Training	Gain	0.9001	2.235
	Phase	0.6887	3.945
	Gain+Phase	0.8805	2.444
Validation	Gain	0.5744	4.894
	Phase	0.4322	5.954
	Gain+Phase	0.6380	4.386

**Table 9. Predicting Calcium Nitrate concentration in blends of three salt solutions**

Data set		R-square	RMSE (ppm)
Training	Gain	0.9025	2.207
	Phase	0.8278	2.934
	Gain+Phase	0.8757	2.493
Validation	Gain	0.6488	4.447
	Phase	0.5663	4.727
	Gain+Phase	0.6464	4.220

**Table 10. Predicting Ammonium Nitrate concentration in blends of three salt solutions**

Data set		R-square	RMSE (ppm)
Training	Gain	0.9704	1.217
	Phase	0.9564	1.476
	Gain+Phase	0.9632	1.357
Validation	Gain	0.8794	2.817
	Phase	0.8828	2.943
	Gain+Phase	0.8960	2.819

It can be seen from Tables 7-10 that the prediction result is better for nitrate than for the potassium, calcium, and ammonium ions. This is probably because that nitrate is the only anion in the mixed solutions, whereas all other ions are all cations. It is more difficult to discriminate between same types of ions because their roles in ionic conduction are similar. However, more accurate detection of individual types of ions is possible if “signature frequencies” for individual ion types are identified. We will further work in this area.

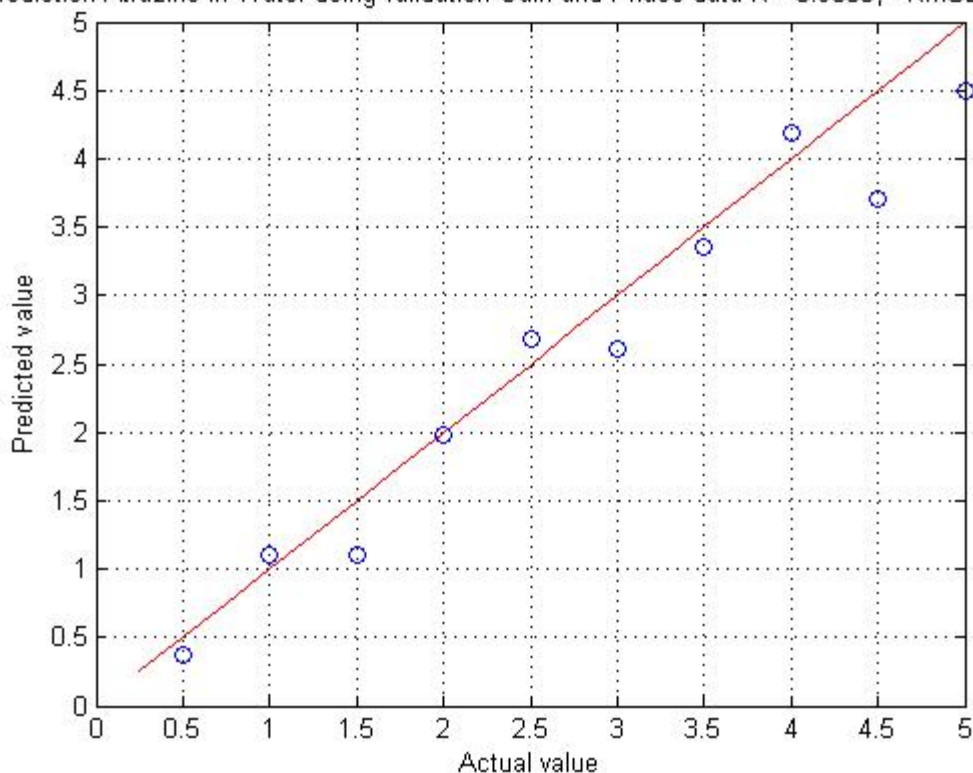
#### 4. Measuring atrazine concentration in water

Water solutions of atrazine at 10 concentrations (0-5 ppm) were tested using the sensor. Two sets of samples were prepared for training and validation purposes, respectively. Results shown in Table 11 and Figure 9 are promising.

**Table 11. Predicting Ammonium Nitrate concentration in blends of three salt solutions**

Data set		R-square	RMSE (ppm)
Training	Gain	0.9949	0.103
	Phase	1.0000	0.001
	Gain+Phase	1.0000	0.002
Validation	Gain	0.9694	0.396
	Phase	0.9456	0.375
	Gain+Phase	0.9558	0.365

Prediction Atrazine in Water using validation Gain and Phase data  $R^2=0.9558$ ,  $RMSE=0.3652$



**Figure 9. Predicted and actual atrazine concentrations (ppm) in deionized water for the validation data set.**

#### **Publications and Presentations**

Zhang, N. 2007. Invited speech: “The potential of a novel frequency-response permittivity sensor in measuring soil and water properties”. Proceedings of the Dahlia Greidinger Symposium 2007, “Advanced Technologies for Monitoring Nutrient and Water Availability to Plants”. March 12-13, Haifa, Israel.

#### **Information Transfer**

U.S. Patent (Pending):

Zhang, N. “Frequency-response sensors and associated signal conditioning/processing for real-time and simultaneous measurement of multiple properties of dielectric materials”, 2007.

#### **Student Support**

Ning Tang: Graduate Research Assistant, studying for M.S. degree in BAE.