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Spectroscopic Measurement of NaCl and Seawater Salinity in the Near-IR Region of 680–1230 nm

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Near-IR Spectroscopic Measurement of Seawater Salinity

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Seawater salinity has been determined by near-IR spectroscopy based on the perturbations of water bands by sea salts. The measurements are made using a cuvette or a fiber-optic probe. The models expressing the salinity are developed by linear or multilinear regression of the absorbances at selected wavelengths and by principal component regression using the entire spectra. Temperature has a strong effect on the water bands and will interfere with the measurement of salinity. However, this effect can be removed by using the absorbances at isosbestic points in the linear model, or it can be accounted for by principal component regression. A standard error of 0.22‰ is attainable by this method. This technique can potentially be used in remote sensing of seawater salinity.

Introduction

Seawater salinity is one of the most important parameters in oceanography. Electrically based conductivity methods have been used to determine seawater salinity for a long time (1). These methods have been well developed and give a high precision ($\pm 0.001\%$). However, they have some drawbacks such as difficulty in the calibration, pressure-induced shifts and hysteresis, and inability to be adapted for remote sensing. Due to the limitations with the conductivity methods, optical approaches have been investigated as alternative techniques for the measurement of salinity. The refractive index measured with a refractometer, an interferometer, and a fiber-optic probe has been used to describe salinity of seawater (2-6). Raman scattering has been used to remotely sense salinity and temperature of seawater (7, 8).

The near-IR spectra of water and aqueous solutions have been extensively studied (9, 10). The perturbations of near-IR water bands by electrolytes are well-known and have been used for the measurement of electrolytes in aqueous solutions (11-15). However, determination of seawater salinity by near-IR spectroscopy has not been reported.

Seawater is an aqueous solution containing a variety of electrolytes (sea salts) (16). Each of the salts perturbs the near-IR water bands and contributes to the total changes in the spectrum of seawater. The pattern and intensity of the perturbations caused by each salt are determined by its ions and their concentrations. The major components (concentrations $> 10^{-4}$ mol/kg) accounting for more than 99.99% of the total sea salts make the largest contributions to the total perturbations. The perturbations caused by the minor components ($< 10^{-4}$ mol/kg) should be insignificant compared to those by the major components. The major components of seawater bear a constant ratio to each other within certain limits (known as "constancy of composition") (17). This makes seawater like an aqueous solution of a single electrolyte with respect to the perturbations on the near-IR water bands. There-

fore, the salinity of seawater can be determined as a "single component".

In this study, seawater salinity was determined by near-IR spectroscopy. The measurements were made employing a cuvette at different temperatures and a fiber-optic probe at room temperature. Models expressing the salinity were developed by linear or multilinear regression of the absorbances at selected wavelengths and by principal component regression using the entire spectra.

Experimental Section

Standard Seawater Samples. A set of 35 seawater samples with known salinities were prepared by weight with a standard seawater and Milli-Q water. A standard seawater sample (Standard Seawater Service, Institute of Oceanographic Sciences, Surrey, England) with a salinity of 35.001‰ was used. The salinities of the seawater samples ranged from 1 to 35‰ at an increment of about 1‰.

Measurement with a Cuvette. The seawater samples were contained in a cuvette having a path length of 2 mm. The near-IR spectra were measured on a NIRSystem Model 6250 spectrophotometer (NIRSystem Inc., Silver Spring, MD). The spectra were scanned from 1100 to 2500 nm; 20 scans were averaged for each spectrum. The spectrometer has an optical resolution of 10 nm and a data point resolution of 2 nm. The temperature of seawater samples at room temperature was about 23.0 °C (± 0.5 °C). The cuvette holder in the spectrometer consisted of a constant temperature block (28.5 °C). Therefore, there was an increase in the temperature of seawater sample after the cuvette was placed in the holder. Equilibrium temperature was reached within about 5 min. Five spectra were measured for each seawater sample beginning at 0, 0.5, 1.0, 2.0, and 7.0 min after the cuvette was placed in the holder. During the time period of the measurements, the temperature of the sample increased from 23.0 to 28.5 °C, but the intermediate temperatures remained unknown. The spectra were measured at different temperatures in order to study the effect of temperature on the determination of the salinity.

Measurements with a Fiber-Optic Probe. A fiber-optic probe for remote measurement was made in-house (15). The optical fibers were Anhydroguide-PCS from Fiberguide Industries (Stirling, NJ). Two fibers were arranged in coaxial and face-to-face position across an indentation on a plexiglass plate with a cell in the center. A gap of about 1 mm was left between the two fiber ends, which served as a light path for seawater samples. A small amount (about 0.3 mL) of the sample was pipetted into the cell of the probe and the spectrum measured at room temperature (23.0 ± 0.5 °C). Spectra were measured for three aliquots of each sample in order to account for possible interferences caused by small fluctuations in room temperature. The spectral measurements were made on a Bio-Rad FTS-40N near-IR spectrometer with an InAs (indium antimonide) detector (Bio-Rad, Digilab Division, Cambridge, MA). Spectra were scanned from 5350 to 9000 cm^{-1} with a resolution of 16 cm^{-1} ; 64 scans were averaged

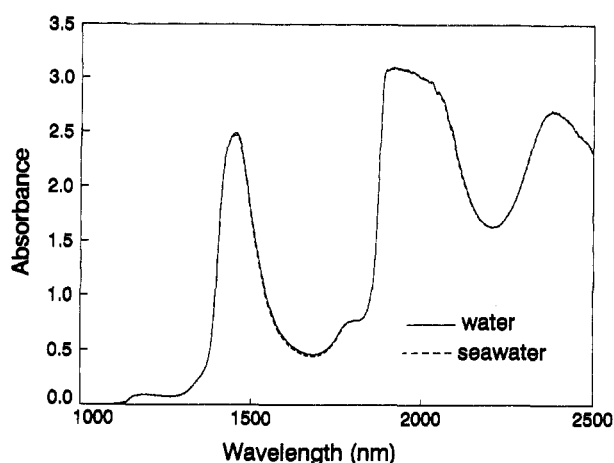


Figure 1. Near-IR spectra of water and 35‰ seawater measured with a cuvette at 28.5 °C.

for each spectrum. The details of the optical attachment and measurement configuration can be found elsewhere (18).

Data Processing. The models expressing the salinity were developed with linear or multilinear regression using absorbances at selected wavelengths and principal component regression using the entire spectra. At least three spectra were measured for each sample; one of the spectra for each sample was randomly selected and used in the unknown (validation) set, and the remainder were used in the standard (training) set. The standard set was used to develop the models which were used to predict the unknown set.

The algorithm used for the principal component regression (PCR) employed successive average orthogonalization developed by Donahue and Brown (19). Multilinear regression (MLR) was performed using a stepwise algorithm (20); four "passes" of the data were performed for the selection of an optimum set of analytical wavelengths. In linear regression models, in which absorbance at one selected wavelength was used, the spectra were baseline zeroed at 1100 nm (or 9000 cm^{-1}) to remove the possible baseline shift. In MLR and PCR, however, the original spectra were used, and the baseline shift was accounted for by the models.

Results and Discussion

Perturbations of Water Bands by Sea Salts. Near-IR spectra of water and 35‰ seawater are shown in Figure 1. Decreases in the absorbances are found over some spectral regions. The differences can be easily seen using a difference spectrum of seawater minus water (spectrum 1 in Figure 2). The perturbations are very clear and are negative over most of the spectral region. The decrease in the absorbance is attributed to a decrease in the concentration of water in seawater and the hydration of the ions of sea salts. The difference spectrum from 1900 to 2500 nm is noisy, resulting from the subtraction of two large absorbances due to water, and is not shown.

A difference spectrum of 1 M NaCl solution minus water is also shown in Figure 2 (spectrum 2) for comparison with that of 35‰ seawater. It can be seen that the shapes of the two difference spectra are similar because NaCl is the major salt in seawater (about 86.5% of the total sea salts in terms of concentration in mol/kg). However, the relative peak heights of the two negative bands at about 1400 and

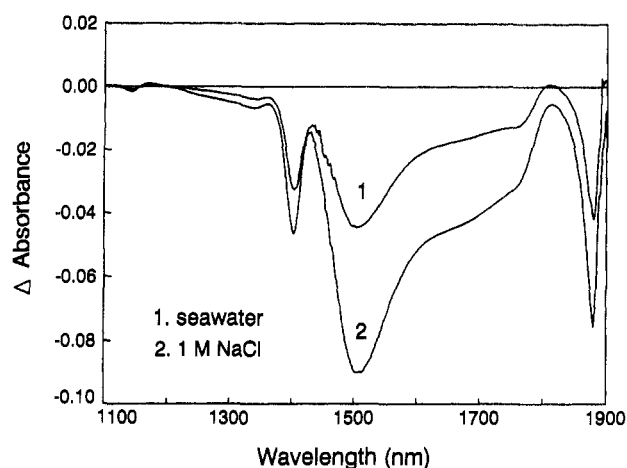


Figure 2. Near-IR difference spectra of 35‰ seawater and 1 M NaCl solution measured using a cuvette at 28.5 °C, with water spectrum as a reference.

Table I. Major Ions and Their Concentrations in a 35‰ Seawater^a

cation	mol/kg	anion	mol/kg
Na ⁺	0.4685	Cl ⁻	0.54591
Mg ²⁺	0.05308	SO ₄ ²⁻	0.02823
Ca ²⁺	0.01028	Br ⁻	0.000842
K ⁺	0.0102	B ⁻	0.00042
Sr ²⁺	0.000090	F ⁻	0.000068

^a The concentrations (in mol/kg of seawater) are calculated from Table 6.1 in ref 16. According to ref 21, in a seawater at pH 8.3 and 10 °C, the concentrations of HCO₃⁻, CO₃²⁻, and B(OH)₄⁻ are 20×10^{-4} , 2.0×10^{-4} , and 1.0×10^{-4} mol/L, respectively. ^b In seawater, one of the major species of boron is B(OH)₄⁻.

1500 nm are not identical in the two spectra. The ratio of the latter to the former is almost 2 for NaCl solution, but it is only 1.35 for seawater. This difference is due to the perturbations caused by the other major salts in seawater.

As indicated in the introduction section, the major components (ions) with high concentrations make the major contributions to the total perturbations of the water bands. The major ions and their concentrations in a 35‰ seawater sample are listed in Table I. Difference spectra of relevant electrolytes (at a concentration of 0.5 M) are shown in Figure 3. It can be seen that different electrolytes perturb the water bands to form different patterns and to different degrees. The shapes of some difference spectra are similar while others are very different. Some of the salts, such as KCl and NaBr, have difference spectra very similar to that of NaCl, whereas CaCl₂ and SrCl₂ have spectra only slightly different from that of NaCl. Surprisingly, those of NaF and MgCl₂ are significantly different. The difference spectra of the oxo-acid sodium salts are completely different from that of NaCl. It can be found that all of these salts cause negative perturbations for wavelengths shorter than 1450 nm. However, the perturbations by some of the salts are less negative than those by NaCl or are even positive in the spectral region of 1500–1900 nm. The negative perturbations by NaCl are offset by the positive perturbations caused by some of the other salts. Therefore, the intensity of total perturbations for seawater are lower than that of NaCl in the latter spectral region.

Calculation of Salinity by Linear Regression. In the above, we discussed the shape of perturbations, and

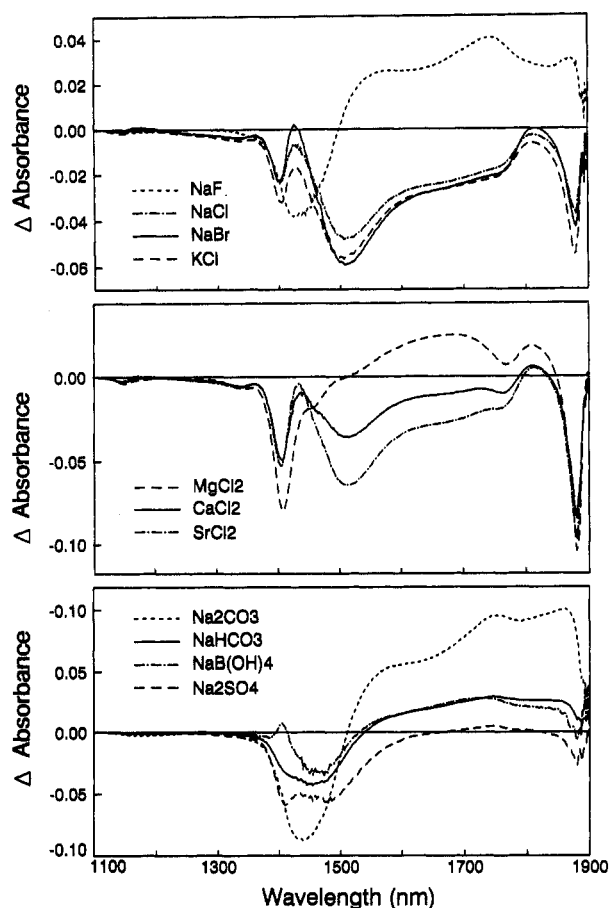


Figure 3. Near-IR difference spectra of 0.5 M solutions of some electrolytes minus water measured with a cuvette at 28.5 °C.

now we will focus on the intensity of the perturbations for the determination of seawater salinity. Figure 4 shows difference spectra of seawater with increasing salinity measured at the same temperature with the spectra of water as the reference. For the measurements made with cuvette, the spectra were measured at 28.5 °C (Figure 4A). It is apparent that the changes in the absorbances at selected wavelengths are reasonably linear with salinity. The model expressing the salinity can be developed by the linear regression (LR) of the absorbances at selected wavelengths. The spectral region which gives SEEs (standard error of estimation) smaller than 0.5‰ is shown in Figure 5. The best linear regression is obtained at 1510 and 1568 nm (while the maximum perturbations occur at 1502 nm). The SEEs obtained are 0.423 and 0.419‰, respectively.

For the measurements made with the fiber-optic probe, the spectra were measured at about 23.0 ± 0.5 °C. The difference spectra are shown in Figure 4B. As can be seen, the features of the difference spectra are complicated compared to those for the measurements made with a cuvette. There are several reasons for this: (1) room temperature was not very constant, and small changes in the temperature would cause significant changes in the spectra; (2) a positive band at 1450 nm was found in the difference spectra measured with the fiber-optic probe, which did not occur for the measurements with the cuvette; (3) larger noise in absorbance appeared in the difference spectra measured with the fiber-optic probe because the path length was only 1 mm (compared to 2 mm of the cuvette). The low light throughput may be another contributing factor to the noisier spectra measured with

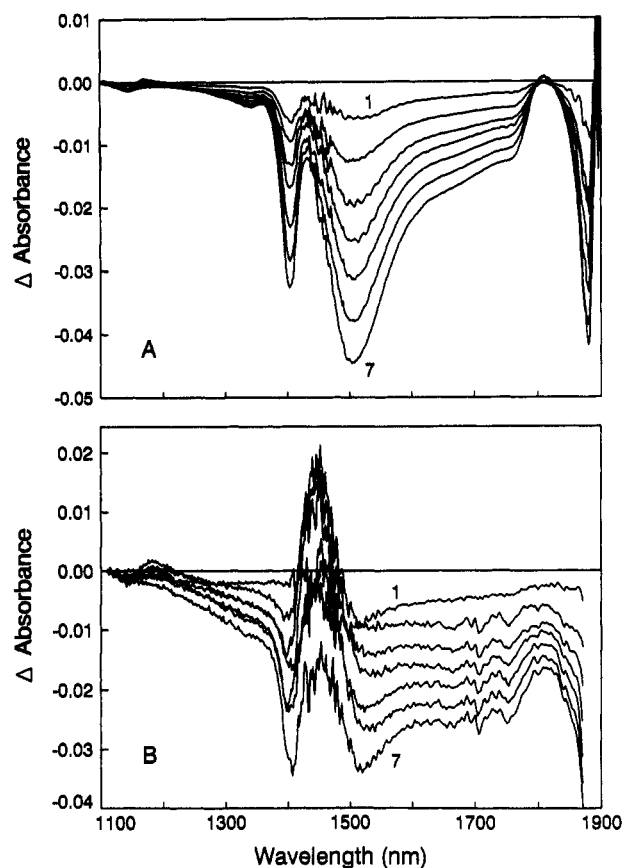


Figure 4. Near-IR difference spectra of seawaters with water spectra as a reference. (A) Measurement with a cuvette at 28.5 °C; (B) measurement with a fiber-optic probe at room temperature (23.0 ± 0.5 °C). Salinity 5, 10, 15, 20, 25, 30, and 35‰ for spectra from 1 to 7.

the probe. The difference spectra are noisy, and the linearity between the change in the absorbance and salinity is obviously not good at most of the spectral region. Therefore, the linear regression (LR) model for salinity was not applied to the measurements made with the fiber-optic probe.

Effect of Temperature on Salinity Measurement. For measurements made with the cuvette, five spectra were scanned for each seawater sample at different temperatures. The difference spectra for 35‰ seawater are shown in Figure 6; the spectrum measured at 28.5 °C was used as the reference. As seen, the change of temperature over 23.0–28.5 °C has a significant effect on the near-IR spectra of seawater.

The effect of temperature on the near-IR spectrum will interfere with the measurement of salinity using the absorbances at selected wavelengths. Fortunately, there are several wavelengths at which the effects of temperature are zero (so called isosbestic points). At two of these wavelengths (1442 and 1782 nm), the changes in the absorbances caused by the sea salts are still large. Therefore, the absorbances at these two isosbestic wavelengths can be used to calculate salinity with a linear regression model (LR_{iso}). The SEEs are 1.811 and 1.464‰, and SEPs (standard errors of prediction) are 1.754 and 1.501‰, respectively.

The standard errors produced in this way are larger than those obtained using the spectra measured at the same temperature. This probably indicates that the temperature effects can not be completely removed by

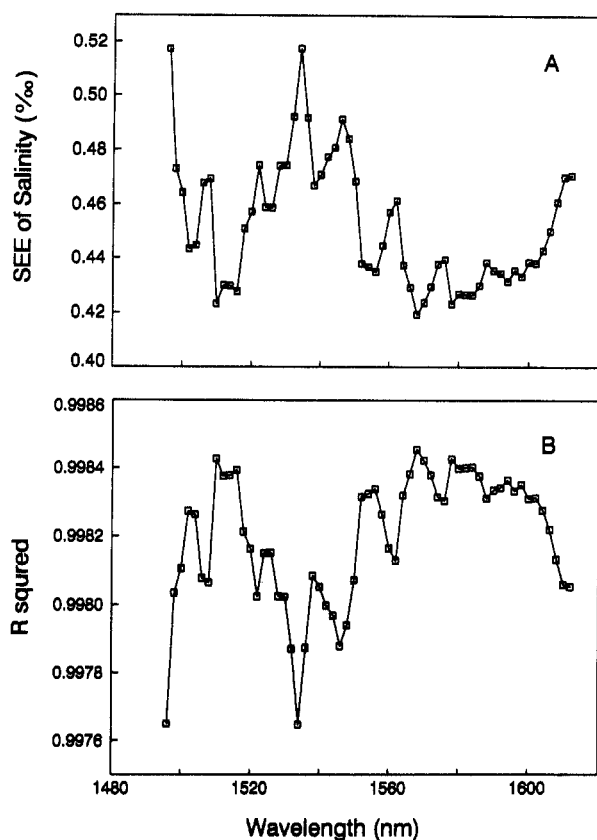


Figure 5. Results for the estimation of salinity by linear regression using the absorbances at selected wavelength. (A) Standard error of estimation (SEE); (B) The squared coefficient of linear correlation. Measurement with a cuvette at 28.5 °C.

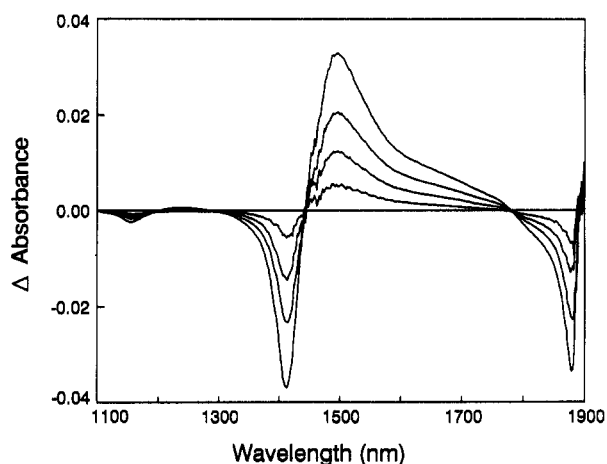


Figure 6. Near-IR difference spectra of 35‰ seawater measured at different temperatures (from 23.0 to 28.5 °C) using a cuvette, with the spectrum measured at 28.5 °C as a reference.

using the absorbance at a single wavelength. In addition, the changes in the absorbances at 1442 and 1782 nm are only about one-third and one-sixth of the maximum perturbations, respectively. This is another reason leading to the larger SEEs. The results of LR_{iso} using absorbance at 1782 nm are better than those at 1442 nm, because the absorbance at 1782 nm is less dependent on the temperature.

Calculation of Salinity by PCR and MLR Models. As discussed above, when the spectra were measured at the same temperature, salinity can be calculated by linear regression models (LR) using the absorbances at one selected wavelength in some spectral regions. When the

Table II. Overall Results for Measurements of Seawater Salinity^a

	SEE	SEP	$S_{NIR} = aS_{ACT} + b$		
a			b	R^2	
	Cuvette				
LR (1510 nm)	0.423				
LR (1568 nm)	0.419				
LR _{iso} (1442 nm)	1.811	1.754	1.0026	-0.018	0.97070
LR _{iso} (1782 nm)	1.464	1.501	1.0012	0.023	0.97834
PCR ($n = 2$)	0.266	0.221	1.0044	-0.104	0.99955
MLR ($n = 5$) ^A	0.440	0.480	0.99821	0.086	0.99779
	Probe				
PCR ($n = 4$)	0.297	0.305	0.99594	0.129	0.99907
MLR ($n = 4$) ^B	0.849	0.863	1.0083	-0.043	0.99258
	Analytical Wavelengths for MLR Model				
A. 1138.0	1396.0	1565.0	1780.0	1872.0	
B. 1399.7	1705.4	1830.7	1870.3		

^a S_{NIR} = near-IR predicted salinity, S_{ACT} = actual salinity. *a*, *b*, and R^2 are the slope, intercept, and squared correlation coefficient for the linear regression of S_{NIR} vs S_{ACT} .

measurements were made at different temperatures, however, only the absorbances at the isosbestic points for temperature effect can be used in the linear regression models (LR_{iso}) to calculate the salinity. At these two wavelengths, the changes in the absorbances caused by salinity are much smaller than the maximum; therefore, the sensitivity and the precision of the measurement decrease. For the measurements made with the fiber-optic probe, the difference spectra are noisy and complicated. A good linear regression model is not likely to be obtained using the absorbances at selected wavelengths. To overcome these problems, we performed the principal component regression (PCR) and multilinear regression (MLR).

The PCR was performed using different spectral regions; the region of 1100–1875 nm (or 9000–5350 cm⁻¹) gave the best results. Two and four eigenvectors are indicated in PCR for the measurements with the cuvette and the probe, and SEPs obtained are 0.221 and 0.305‰, respectively. For the measurements with the cuvette, two variables (i.e., salinity and temperature) are encountered. Only two eigenvectors are indicated in the PCR model, implying that other variables are very insignificant. For the MLR model, the optimum analytical wavelengths were selected in the region of 1100–1875 nm (or 9000–5350 cm⁻¹). Five and four wavelengths are needed for the measurements with the cuvette and the probe; SEPs produced are 0.480 and 0.863‰, respectively.

Comparison of Overall Results. All the results for different measurements and from different models are summarized in Table II. Several points should be made from a comparison of the results in this table. (1) Better results are obtained for the measurements with the cuvette. This is likely due to the facts that the light throughput is larger and that the light path length is longer for the cuvette than for the probe (2 vs 1 mm). (2) The smallest SEEs and SEPs are obtained by the PCR model, because PCR employed the successive average orthogonalization which will increase the “effective” signal-to-noise ratios (by averaging). (3) For the spectra measured at a constant temperature with the cuvette, the LR model using absorbance at one wavelength (with baseline zeroed at another wavelength) gives very similar SEEs to those obtained in MLR using absorbances at five wavelengths for the spectra measured at different temperatures.

The spectra measured with the 2-mm cuvette have absorbances above 2 AU in the region of 1412–1492 nm. There may be a concern that the absorbance is not linear with salinity in this region. The LR and MLR models do not select wavelengths in this region. The PCR model can account for nonlinearity in absorbance by using extra eigenvectors. Only two eigenvectors are indicated in the PCR model for the variations of salinity and temperature. This means that the part of the spectra with absorbance above 2 AU does not have a significant impact on the PCR model. In the LR_{iso} model, however, a good linear regression is obtained between the salinity and the absorbance at 1442 nm. This indicates that the absorbance may be linear with the salinity at above 2 AU.

The linear correlations between near-IR predicted salinity (S_{NIR}) and actual salinity (S_{ACT}) were made, and the results are also listed in Table II. As seen, very good linear correlations are produced. The slopes are very close to 1, and the intercepts are very small ($b \ll SEP$). Overall, the best correlations are obtained for the results from the PCR model.

Potential Applications of Present Method. The smallest standard error obtained with near-IR spectroscopy in this study is 0.22‰. This accuracy is not as good as that attainable with the conductivity methods. Thus, the present method cannot replace the conductivity methods. For open ocean seawater, for which an accuracy of $\pm 0.001\%$ is required, the near-IR method is not applicable. However, for the measurement of salinity in an estuarine and coastal area where the salinity may vary from 0 to higher than 30‰, the near-IR method can be applied.

The near-IR method has two major advantages over the conductivity methods, i.e., the simplicity in the calibration and the possibility of being used for remote sensing. For the near-IR method, the drift (in baseline) can be offset by zeroing the spectra at a specific wavelength, and intermediate calibration is not needed during the course of the measurement. By means of a fiber-optic probe, the real-time measurement can be made *in situ*. With the success in the remote sensing of the surface temperature of seawater, there is possibility that near-IR spectroscopy can be adapted for remote sensing of the salinity of surface seawater.

In another study, we have used a similar fiber-optic probe for the simultaneous measurement of NaCl and temperature in aqueous solution over 0–2 M and 15–35 °C (15). Therefore, there is no doubt that both salinity and temperature of seawater can be measured simultaneously with a fiber-optic probe. A sea-going device for the measurements of salinity and temperature can be developed.

Conclusions

Seawater salinity has been determined by near-IR spectroscopy based on the perturbations of the water band by the sea salts. The salinity can be calculated by the linear or multilinear regression of the absorbances at selected wavelengths or the principal component regression using the entire spectra. Standard error of 0.22‰ is attainable for salinity in the range of 0–35‰. The measurement can be made with a cuvette in the laboratory or with a fiber-optic probe on-board a ship.

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