Standard Methods for the Examination of Water and Wastewater

2520   SALINITY*#(1)

2520 A.   Introduction

1. General Discussion

Salinity is an important unitless property of industrial and natural waters. It was originally conceived as a measure of the mass of dissolved salts in a given mass of solution. The experimental determination of the salt content by drying and weighing presents some difficulties due to the loss of some components. The only reliable way to determine the true or absolute salinity of a natural water is to make a complete chemical analysis. However, this method is time-consuming and cannot yield the precision necessary for accurate work. Thus, to determine salinity, one normally uses indirect methods involving the measurement of a physical property such as conductivity, density, sound speed, or refractive index. From an empirical relationship of salinity and the physical property detemined for a standard solution it is possible to calculate salinity. The resultant salinity is no more accurate than the empirical relationship. The precision of the measurement of a physical property will determine the precision in salinity. Following are the precisions of various physical measurements and the resultant salinity presently attainable with commercial instruments:

Property	Precision of Measurement	Precision of Salinity
Conductivity	±0.0002	±0.0002
Density	$\pm 3 \times 10^{-6}$ g/cm^3	±0.004
Sound speed	±0.02 m/s	±0.01

Although conductivity has the greatest precision, it responds only to ionic solutes. Density, although less precise, responds to all dissolved solutes.

2. Selection of Method

In the past, the salinity of seawater was determined by hydrometric and argentometric methods, both of which were included in previous editions of *Standard Methods*. In recent years the conductivity (2520B) and density (2520C) methods have been used because of their high sensitivity and precision. These two methods are recommended for precise field and laboratory work.

3. Quality Assurance

Calibrate salinometer or densimeter against standards of KCl or standard seawater. Expected

precision is better than ±0.01 salinity units with careful analysis and use of bracketing standards.

2520 B. Electrical Conductivity Method

1. Determination

See Conductivity, Section 2510. Because of its high sensitivity and ease of measurement, the conductivity method is most commonly used to determine salinity.[1] For seawater measurements use the Practical Salinity Scale 1978.[2-5] This scale was developed relative to a KCl solution. A seawater with a conductivity, C, at 15°C equal to that of a KCl solution containing a mass of 32.4356 g in a mass of 1 kg of solution is defined as having a practical salinity of 35. This value was determined as an average of three independent laboratory studies. The salinity dependence of the conductivity ratio, R_t, as a function of temperature (t °C, International Practical Temperature Scale 1968) of a given sample to a standard $S= 35$ seawater is used to determine the salinity

$$S = a_0 + a_1 R_t^{1/2} + a_2 R_t + a_3 R_t^{3/2} + a_4 R_t^2 + a_5 R_t^{5/2} + S$$

where S is given by

$$\Delta S = \left[\frac{t - 15}{1 + 0.0162 (t - 15)} \right] (b_0 + b_1 R_t^{1/2}$$
$$+ b_2 R_t + b_3 R_t^{3/2} + b_4 R_t^2 + b_5 R_t^{5/2})$$

and:

$a_0 = 0.0080$	$b_0 = 0.0005$
$a_1 = -0.1692$	$b_1 = -0.0056$
$a_2 = 25.3851$	$b_2 = -0.0066$
$a_3 = 14.0941$	$b_3 = -0.0375$
$a_4 = -7.0261$	$b_4 = 0.0636$
$a_5 = 2.7081$	$b_5 = -0.0144$

valid from $S = 2$ to 42, where:

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$$R_t = \frac{C \text{ (sample at } t)}{C \text{ (KCl solution at } t)}.$$

To measure the conductivity, use a conductivity bridge calibrated with standard seawater*#(2) with a known conductivity relative to KCl, following manufacturer's instructions and the procedures noted in Section 2510. If the measurements are to be made in estuarine waters, make secondary calibrations of weight-diluted seawater of known conductivity to ensure that the bridge is measuring true conductivities.

The Practical Salinity Scale recently has been extended to low salinities[6] to give an equation that is valid from 0 to 40 salinity. The equation is:

$$S = S_{PSS} - \frac{a_0}{1 + 1.5X + X^2} - \frac{b_0 f(t)}{1 + Y^{1/2} + Y^{3/2}}$$

where:

S_{PSS} = value determined from the Practical Salinity Scale given earlier,
a_0 = 0.008,
b_0 = 0.0005,
$X = 400R_t$,
$Y = 100R_t$, and
$f(t) = (t-15)/[1 + 0.0162\,(t-15)]$

The practical salinity breaks with the old salinity-chlorinity relationship, $S = 1.806\,55\ Cl$. Although the scale can be used for estuarine waters[7-10] and brines[11-13], there are limitations.[12,14-22]

2. References

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2520 C.   Density Method

1. Determination

With a precise vibrating flow densimeter, it is possible to make rapid measurements of the density of natural waters. The measurements are made bypassing the sample through a vibrating tube encased in a constant-temperature jacket. The solution density (ρ) is proportional to the square of the period of the vibration (τ).

$$\rho = A + B\tau^2$$

where *A* and *B* are terms determined by calibration, *B* being determined by calibration with a densimeter with standard seawater. The difference between the density of the sample and that of pure water is given by:

$$\rho - \rho_0 = B(\tau^2 - \tau_0{}^2)$$

where τ and τ_0 are, respectively, the periods of the sample and water. The system is calibrated with two solutions of known density. Follow manufacturer's recommendations for calibration. These two solutions can be nitrogen gas and water or standard seawater and water. The salinity of the sample can be determined from the 1 atm international equation of state for seawater. This equation relates ($\rho - \rho_0$) to the practical salinity (*S*) as a function of temperature.[1]

$$\rho \ (kg/m^3) = \rho_0 + AS + BS^{3/2} + CS^2$$

where:

$$A = 8.244\ 93 \times 10^{-1} - 4.0899 \times 10^{-3}t$$
$$+ 7.6438 \times 10^{-5}t^2 - 8.2467 \times 10^{-7}t^3 + 5.3875 \times 10^{-9}t^4,$$
$$B = -5.724\ 66 \times 10^{-3} + 1.0227 \times 10^{-4}t - 1.6546 \times 10^{-6}t^2,$$
$$C = 4.8314 \times 10^{-4},$$

and the density of water is given by:

$$\rho_0 = 999.842\ 594 + 6.793\ 952 \times 10^{-2}t - 9.095\ 290 \times 10^{-3}\ t^2$$

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$$+ 1.001\,685 \times 10^{-4}\,^3 \quad 1.120\,083 \times 10^{-6}\,^4 + 6.536\,332$$
$$^{-9}t$$

Perform simple iteratio $\quad$ *S* until it gives the measured $\quad - \rho_0$

If the measurements are made at 25°C, the salinity can be determined from the following equation:

$$= 1.3343\,(\rho - {}_0) + 2.155\,306 \times 10 \quad (\rho - {}_0) - \qquad\qquad {}^{-5}(\ -\rho\ )^3$$

as a τ $\qquad$ *S*. Approximate salinities also can be determined from densities or

edition).

2. Reference

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2520 D. Algorithm of Practical Salinity

Because all practical salinity measurements are carried out in reference to the conductivity $S = 35$), it is the quantity $_t$ that will be available for salinity tions. *R* normally is obtained directly by laboratory salinometers, but *in situ*

R, the ratio of the $\qquad$ conductivity to the standard conductivity at $= 35, t \qquad p = 0$ (where is the pressure above one standard atmosphere *R* is factored into three

$$R = {}_p r\, R_t$$

where:

$_p$ = ratio of $\qquad$ conductivity to conductivity of the same sample
at the same tem $\qquad p = 0$ and $_t$ = ratio of

of 35, at temperature *t* $\qquad\qquad t = 15°C$. From
$R_p \qquad r_t \qquad\qquad R_t \qquad$ *in situ* re

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$$R_t = \frac{R}{R_p r_t}$$

R_p and r_t can be expressed as functions of the numerical values of the *in situ* parameters, *R, t,* and *p*, when *t* is expressed in °C and *p* in bars (10^5 Pa), as follows:

$$R_p = 1 + \frac{p(e_1 + e_2 p + e_3 p^2)}{1 + d_1 t + d_2 t^2 + (d_3 + d_4 t)R}$$

where:

$$e_1 = 2.070 \times 10^{-4}, \qquad d_1 = 3.426 \times 10^{-2},$$
$$e_2 = -6.370 \times 10^{-8}, \qquad d_2 = 4.464 \times 10^{-4},$$
$$e_3 = 3.989 \times 10^{-12}, \qquad d_3 = 4.215 \times 10^{-1},$$
$$\text{and} \qquad\qquad\qquad\qquad d_4 = -3.107 \times 10^{-3},$$

and

$$r_t = c_0 + c_1 t + c_2 t^2 + c_3 t^3 + c_4 t^4$$

where:

$c_0 = 0.676\ 609\ 7,$

$c_1 = 2.005\ 64 \times 10^{-2},$

$c_2 = 1.104\ 259 \times 10^{-4},$

$c_3 = -6.9698 \times 10^{-7},$ and

$c_4 = 1.0031 \times 10^{-9}.$

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Endnotes

1 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1993.
2 (Popup - Footnote)
* Available from Standard Seawater Services, Institute of Oceanographic Services, Warmley, Godalming, Surrey, England.