

# On the possibility of application of a polarimetric method for determination of salinity in sea-water\*

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Polarimetric measurement  
Salinity  
Sea-water

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## Abstract

The paper presents static polarimetric method that has been used for measurements of the angle of polarization of synthetic sea-water as a function of the wavelength and salinity. It has been proven that the total rotation angle of the plane of polarization has — in the case of synthetic sea-water — the property of additivity. This fact permits to use the polarimetric method for determining the sea-water salinity. Conditions under which the method may be used are discussed.

## 1. Introduction

The so-called 'practical' definition of sea-water salinity is based on a comparison of the electrolytic conductivity of a sea-water sample with that of a standard solution of KCl (Perkin, Lewis, 1980). Physical oceanographers gradually replaced the definition of salinity involving chlorinity (Knudsen, 1902) by that based entirely on conductivity. In physical oceanography this is an important improvement, but from the point of view of chemists and biologists the salinity satisfying this definition is no longer a true measure of the salt content in sea-water, in particular when estuaries and coastal areas are concerned.

The polarimetric methods are widely used in studies of electronic properties of active molecules, in determining biological polymers, as well as in studies of absorption spectra of polyatomic molecules in the UV region. These methods are also used

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for determination of the circular polarization and the rotation angle of the plane of polarization of mixed lines in magnetic field when determining the quadrupole admixture (Roberts *et al.*, 1980). Various types of polarimeters have been used in these measurements, the most common ones described in the work by Azzam and Baskara (1977).

This work presents a polarimetric system which may be used in studies of low intensity signals and small angles of rotation of the plane polarization. It is a conventional PMSA system (polarizer P, modulator M, measuring system S, linear analyzer A), in which all the optical parts rest motionless. A system similar to that was described previously (Heldt *et al.*, 1984). It was used for determination of the molar rotation angles for the respective salts contained in the synthetic sea-water. It was proven that for the synthetic sea-water of salinity  $S \leq 45\text{‰}$  the total angle of rotation of the polarization plane exhibits the property of additivity, *ie* its value is a sum of those of partial angles of polarization for the components. This result permits to use the polarimetric method described for the salinity determination of sea-water. This was confirmed by tests of a sea-water sample collected from the Gulf of Gdańsk.

## 2. Polarimetric system

The measuring system is shown schematically in Figure 1. Here, the light source is an Ar<sup>+</sup> laser (Carl Zeiss, Jena, ILA-1 type). The laser beam passes through the polarizer P (Glan-Thompson prism), the modulator M (Faraday cell filled with

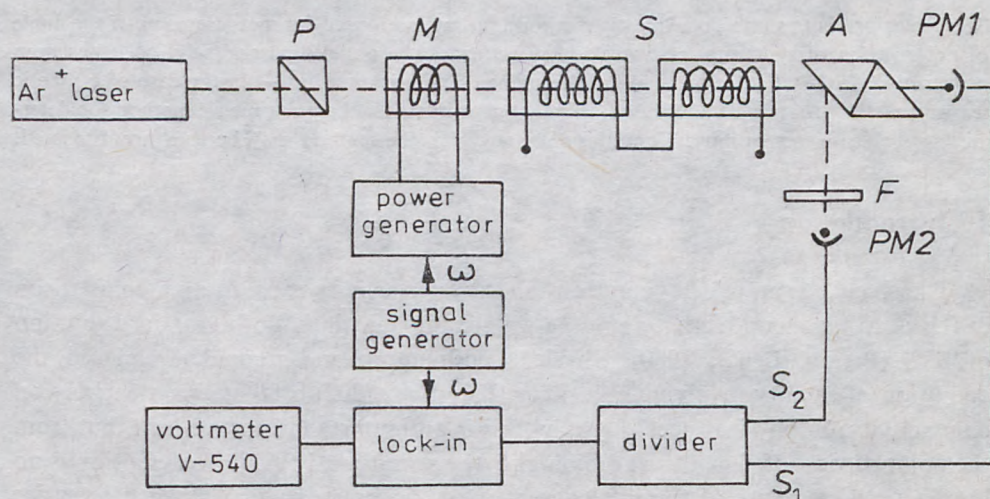


Fig. 1. Diagrammatic arrangement of the polarimetric set-up P—polarizer, M—modulator, S—measuring and compensation cells, A—analyser, PM1 and PM2—photomultipliers, F—light reducer

water), two Faraday cells S (the first one—the measuring cell, the second one—the compensation cell) and the analyser A (Nicol prism). The cylindrical cell of a length  $l=0.15$  m, placed in a solenoid generating a sinusoidally variable magnetic field, was applied as a modulator of polarization. Application of two solenoids wound in



an 'opposite directions' system—made it possible to compensate fully the rotation angle of the plane of polarization of light propagating through the solvent (water). The electric signal ( $S_1$ ) of the photomultiplier PM 1 is proportional to the intensity of light passing through the optical system of polarimeter. The signal  $S_2$ , detected by the photomultiplier PM, 2 is a part of the reference beam reflected from the front side of the Nicol prism. Normalization of the signal  $S_1$  (after dividing its value by  $S_2$ ) is done by a dividing system (Keithley Inst. 301). The rotation angle of the polarization plane of  $Ar^+$  laser beam caused by dissolved salts is determined from the amplitude of the alternating signal of a  $\omega$  frequency (which is the angular frequency of the modulator). As will be shown, the amplitude of this signal is proportional to the measured angle of rotation of the polarization plane.

In the PMSA polarimeter of our design there are no moving optical parts. The device is a modification of the polarimeter described by Roberts *et al.* (1980). The intensity of light incident on the photocatode of the photomultiplier PM 1 in the case of 'crossed' prisms P and A may be written in the following form:

$$I_1 = |E_x^2| + |E_y^2| + DI_0 + \dots, \quad (1)$$

where D is a constant determining the transmission properties of the 'crossed' prisms (in our system  $D = 5 \cdot 10^{-7}$ ) and  $E_x$ ,  $E_y$  are the electric field components of the light beam.

The electric field components are determined by multiplication of the Jones matrices written for all the optical parts of the polarimeter PMSA successively:

$$\begin{bmatrix} E_x \\ E_y \end{bmatrix} = \begin{bmatrix} 1, & 0 \\ 0, & 0 \end{bmatrix} \begin{bmatrix} \cos \delta_M, & -\sin \delta_M \\ \sin \delta_M, & \cos \delta_M \end{bmatrix} \begin{bmatrix} \cos \varphi, & -\sin \varphi \\ \sin \varphi, & \cos \varphi \end{bmatrix} \begin{bmatrix} 0, & 0 \\ 0, & 1 \end{bmatrix} \begin{bmatrix} 0 \\ E_0 \end{bmatrix}, \quad (2)$$

where  $\delta_M = \sin \omega t$  describes modulation of the rotation angle of the plane of polarization (for our modulator  $A_0 = 0.02$  rad and  $\omega = 317$  Hz);  $\varphi$  is the angle of the rotation of the plane of polarization of the light beam passing the solution of dissolved salts. Using the product of the matrices in (2) one may rewrite formula (1) as follows:

$$I_1 = I_0 \left\{ \left[ \frac{1}{2} - \frac{1}{2} (\cos 2\delta_M \cos 2\varphi - \sin 2\delta_M \sin 2\varphi) \right] + D \right\}, \quad (3)$$

where  $I_0$  is the incident beam intensity.

Expansion of functions  $\cos \delta_M$  and  $\sin 2\delta_M$  in a series yields the following equation:

$$I_1 = I_0 \left\{ \left[ \frac{1}{2} - \frac{1}{2} \cos 2\varphi J_0(2A_0) - \cos 2\varphi \sum_{k=1}^{\infty} J_{2k}(2A_0) \cos 2k\omega t \right. \right. \\ \left. \left. + \sin 2\varphi \sum_{k=1}^{\infty} J_{2k-1}(2A_0) \sin(2k-1)\omega t \right] + D \right\}, \quad (4)$$

where  $J_k(2A_0)$  are the Bessel functions.

Limiting the expansion (4) to first order terms and assuming that angles  $A_0$  are small, one may describe the electric output signal of the dividing system by the expression:

$$S_3 = \frac{S_1}{S_2} \sim \frac{I_1}{I_0} \simeq \varphi^2 + 2\varphi A_0 \sin \omega t + A_0^2 \cos 2\omega t + D. \quad (5)$$



The component of frequency  $\omega$  is separated from the signal  $S_3$  by the phase-sensitive detection unit. The amplitude of this component is proportional to the measured rotation angle  $\varphi$ . The signal  $S_3$ , coupled to a lock-in amplifier, does not depend on

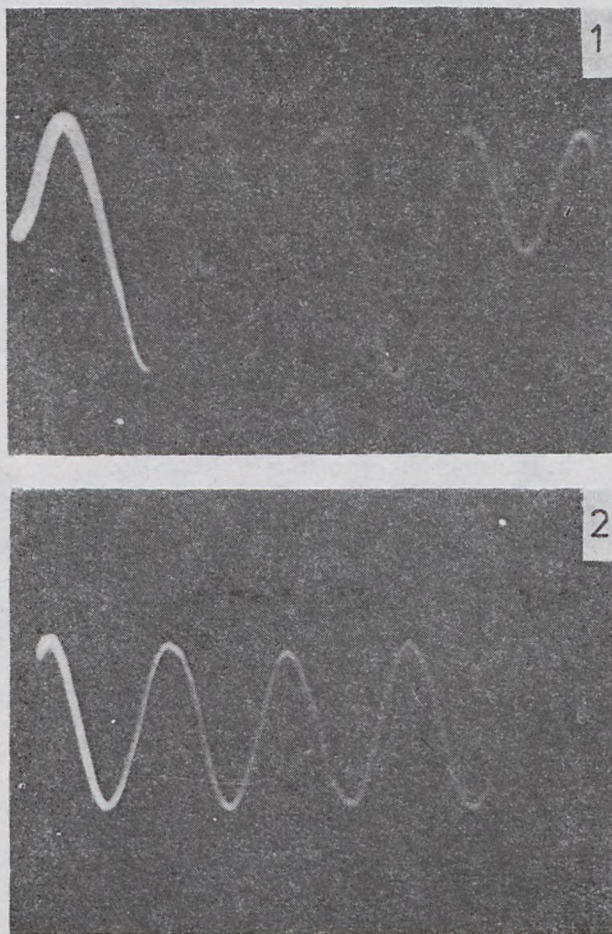


Fig. 2. Oscillograph records of the signals  $S_1/S_2$  recorded at the point B (Fig. 1) at two values of rotation angle  
 1 -  $\varphi = 2 \cdot 10^{-4}$  rad; 2 -  $\varphi = 0$  rad

the light intensity  $I_0$  and is therefore free from fluctuations due to intensity changes of the laser light source. In the PMSA polarimetric system (see Fig. 1) the frequency selection is ensured by a homodyne lock-in amplifier of 232 B type. The reference signal for the lock-in amplifier ( $\omega = 317$  Hz) is taken from the generator G.

Examples of oscillograms of  $S_3$  signals are shown in Figure 2. They were recorded at two values of the rotation angle  $\varphi$ . Calibration of the polarimeter was carried out for the cell  $S$  filled with water. The Verdet constant of water and dispersion of the cell are known from literature (Kaye *et al.*, 1973).



### 3. Reagents and solutions

The salts used in our investigations (reagent grade, from POCh Gliwice) were additionally crystallized twice from redistilled water. Stock solutions were prepared by dissolving the recrystallized salts in redistilled water. Solutions of the ionic medium simulating sea-water (synthetic sea-water) were prepared according to Khoo *et al.* (1977)—see Table 1.

**Table 1.** Composition of the stock ionic medium (synthetic sea-water), corresponding to salinity  $S=45\text{‰}$

Ion	Molarity [mol·(kg H <sub>2</sub> O) <sup>-1</sup> ],
Na <sup>+</sup>	0.69309
Mg <sup>2+</sup>	0.06700
Ca <sup>2+</sup>	0.01308
K <sup>+</sup>	0.0511
Cl <sup>-</sup>	0.81303
SO <sub>4</sub> <sup>2-</sup>	0.03553

The natural sea-water sample of salinity  $S=7.4\text{‰}$ , collected from the Gulf of Gdańsk, was filtered before the measurement; a Whatman GF/C glass-fiber filter was used.

### 4. Measurements

The polarimetric set up, as shown in Figure 1, was used for measurements of the angle of rotation of the plane of polarization of light beam passed through a solution of one of salts—components of the synthetic sea-water, the synthetic sea-water itself, and a natural sea-water sample.

Figure 3 shows the relationship between the rotation angle of the plane of polarization  $\varphi$  and concentration  $c$  [%] of salt for NaCl solution. The measurements were carried out at two wavelengths, constant magnetic field  $B=1.87 \cdot 10^{-2}$  T and a temperature  $T=288$  K, in a cell of active length  $l=0.397$  m.

On the basis of the determined angle of the polarization plane, rotation values of the molar rotation  $\Omega$  [rad·m<sup>2</sup>·T<sup>-1</sup>·mol<sup>-1</sup>·10<sup>-4</sup>] were calculated for individual salts as a function of wavelength:

$$\Omega^{(\lambda)} = \frac{\varphi(\lambda)}{\rho B l}, \quad (6)$$

where  $\rho$  is the molar concentration of the solution [mol·dm<sup>-3</sup>]. The values of molar rotation  $\Omega$  calculated for the studied salts are summarized in Table 2.

Table 3 shows the determined values, as a function of wavelength, of the polarization plane rotation angle  $\varphi_{\text{exp}}$  for the synthetic sea-water of salinity  $S=10\text{‰}$  and



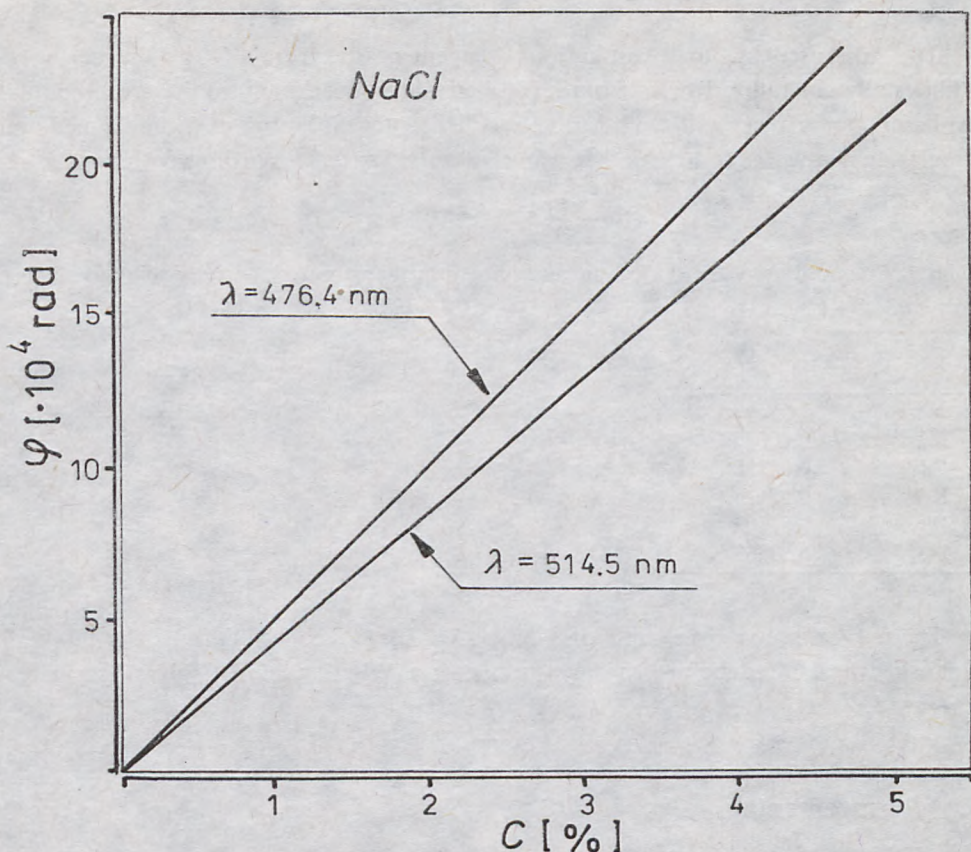


Fig. 3. Relationship between the rotation angle  $\varphi$  and the concentration  $c$  [%] of NaCl solution

Magnetic induction  $B=1.87 \cdot 10^{-2}$  T, cell length  $l=0.397$  m,  $T=288$  K

Table 2. Values of molar rotation for salts—components of the synthetic sea-water

$\lambda$ [nm]	$\Omega \left[ \frac{\text{rad} \cdot \text{m}^2}{\text{T} \cdot \text{mol}} \cdot 10^4 \right]$				
	NaCl	KCl	CaCl <sub>2</sub>	MgCl <sub>2</sub>	MgSO <sub>4</sub>
514.5	3.403	2.880	6.370	6.254	1.512
501.7	3.578	3.025	6.516	6.574	1.570
496.5	3.636	3.112	6.719	6.748	1.575
488.0	3.839	3.287	7.039	7.010	1.658
476.5	4.014	3.461	7.534	7.359	1.678

$S=43,588^{\circ}/_{00}$ , at various values of the magnetic field  $B$ . For a comparison, corresponding angle values calculated on the basis of molar rotation values  $\Omega$  (Table 2) and molar concentrations  $\rho_i$  of the salts contained in sea-water are given in Table 3.

The maximum measurement error did not exceed 5%—radiation losses on the optical parts of the system and the sensitivity of recording devices having been its



**Table 3.** Experimental and calculated values of the angle of rotation of the polarization plane for the synthetic sea-water of  $S=10^0/_{00}$  and  $43.588^0/_{00}$  at different values of the magnetic field induction  $B$  and the measuring cell length  $l$

$\lambda$ [nm]	$\varphi \cdot 10^4$ [rad]		$\varphi_{\text{cal}} - \varphi_{\text{exp}}$
	calculated	experimental	$\varphi_{\text{exp}}$
$B=1.87 \cdot 10^{-2}$ T; $l=0.397$ m; $S=10^0/_{00}$			
514.5	4.136	4.072	0.0158
476.5	4.846	4.858	0.0020
$B=1.31 \cdot 10^{-2}$ T; $l=0.270$ m; $S=43.588^0/_{00}$			
514.5	8.973	8.966	0.0007
476.5	10.138	10.125	0.0013
$B=4.35 \cdot 10^{-2}$ T; $l=0.270$ m; $S=43.588^0/_{00}$			
514.5	29.933	29.906	0.0009
476.5	33.793	33.816	0.0007

main sources. The errors caused by absorption and scattering of light by water in the cells can be neglected since the total attenuation coefficient for water, at the wavelength generated by the  $\text{Ar}^+$  laser, is lower than  $0.04 \text{ m}^{-1}$  (Morel *et al.*, 1977).

## 5. Discussion

For all tested solutions of individual salts, the curves  $\varphi = \varphi(\lambda, B)$  were identical to that obtained for NaCl solution (Fig. 3) which is an agreement with theoretical predictions. The slopes of these curves were different for different salts and wavelengths. According to Heldt *et al.* (1985), the value of  $\varphi$  determined, under conditions that  $l$ ,  $\lambda$ , and  $B$  are *constants*, depends on the molarity of the solution investigated. This finding allows to use the method for measurement of concentration of a known salt in the aqueous solution. The rotation angle  $\varphi$  determined experimentally for the synthetic sea-water was, within the error limits, in agreement with the value calculated as a sum of the respective components:

$$\varphi(\lambda) = \sum_{i=1}^n x_i \Omega_i(\lambda), \quad (9)$$

where  $x_i$  are the mole fractions of the respective salts. This allows us to state that for the salt concentration and applied magnetic field induction ranges covered by our investigations the total rotation angle  $\varphi$  is an additive quantity (see Table 3).

Differences between the values  $\varphi_{\text{exp}}$  and  $\varphi_{\text{calc}}$  (Table 3) for the synthetic sea-water, are smaller than the measuring error and do not exceed the value of 1.6%. The average difference equals to 0.2%.

Assuming that the mass concentration ratios of natural sea-water components correspond to those of synthetic sea-water, we should obtain identical  $\varphi(\lambda, B)$  curves for both the natural and synthetic sea-water. An example of  $\varphi(\lambda)$  obtained for sea-water of salinity  $S=7.4^0/_{00}$  collected from the Gulf of Gdańsk and synthetic sea-water of the same salinity is shown in Figure 4 ( $B=1.87 \cdot 10^{-2}$  T,  $l=0.397$  m). These results permit us to determine the salinity of sea-water by comparing the values of  $\varphi(\lambda)$ ,



measured for known parameters  $B$  and  $l$ , with those taken from an appropriate diagram of  $\varphi(\lambda, S)$ , as presented in Figure 5.

The salinity of the sample collected from the Gulf of Gdańsk, determined at wavelength  $\lambda=476.4$  nm and 514.5 nm was 7.52‰. The difference between the salinity values determined with STD system indications and those obtained by the

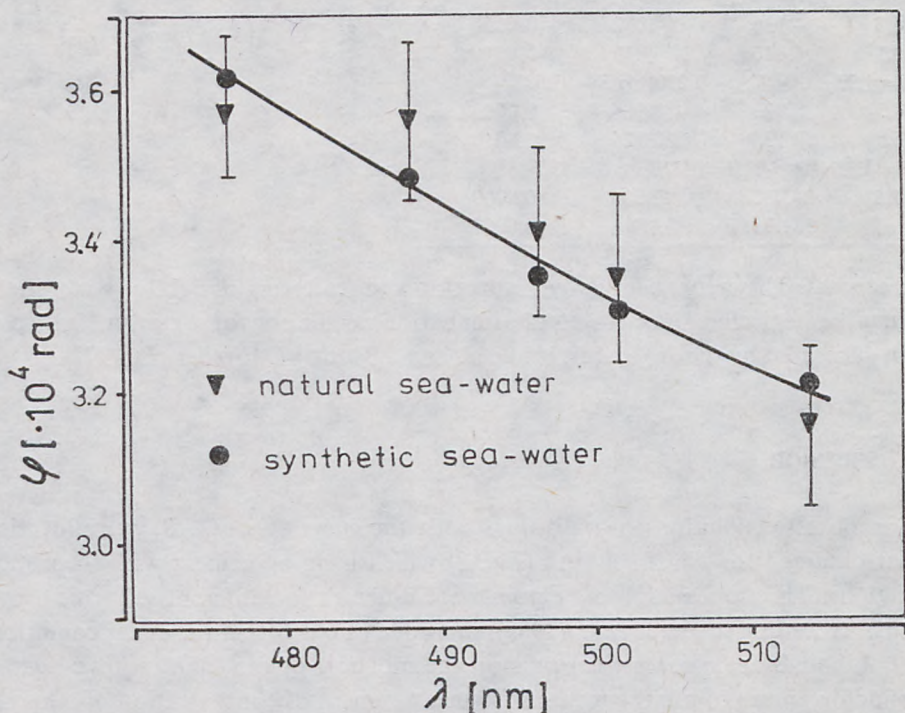


Fig. 4. Rotation angle  $\varphi$  vs wavelength  $\lambda$  for synthetic and natural sea-water samples, both of salinity  $S=7.4$ ‰

polarimetric method was  $\Delta S=0.12$ ‰. When a longer cell  $S$  is used and simultaneously an increase of magnetic field is applied, then the accuracy of measurement is increased up to some limit; according to our estimations, the minimum error value is  $\Delta S \cong 0.05$ ‰. This value is beyond the range of accuracy 0.003‰ determined by a joint panel of UNESCO (1981) on the basis of the practical definition of salinity. However, one should remember that the precision of the conductometric measurements is better than accuracy of the determination of salinity on the basis of the conductometric measurements. The conductometric STD systems do not give the direct answer and require the use of various algorithms in which the pressure and temperature corrections are included. There is also the influence of nonconservative components, especially  $p^{[H^+]}$ ; the nutrient changes alone may affect the salinity in the third decimal place under all circumstances and certainly in the second decimal place in the case of some marine environments.



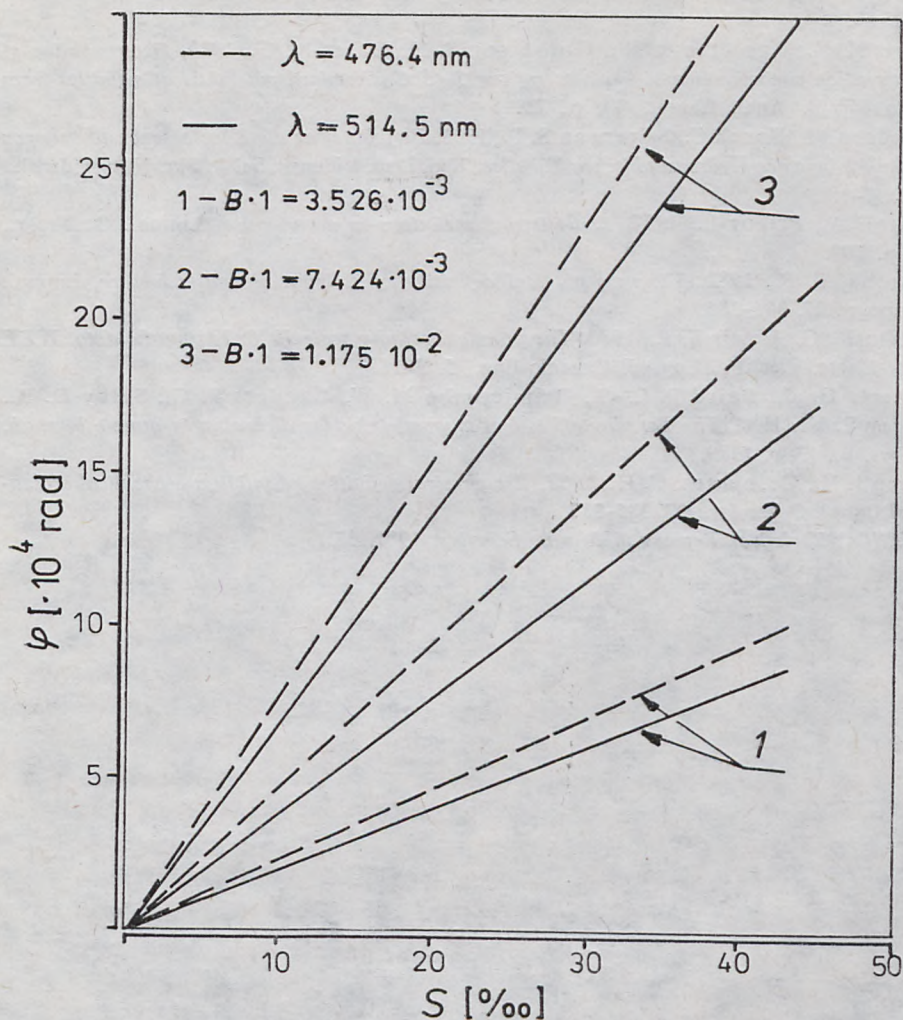


Fig. 5. Relationship between the rotation angle  $\varphi$  [ $10^4$  rad] and the salinity  $S$  [‰]

In view of these facts the accuracy of the polarimetric method is satisfactory. As the polarimetric determination of salinity is simple and immediate the method may be very useful for some purposes.

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