

REMOTE MEASUREMENT OF SEA WATER TEMPERATURE,  
SALINITY AND THICKNESS OF OIL FILM  
USING WATER RAMAN SCATTERING

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ABSTRACT:

In this communication the method of remote measurement of seawater temperature (T), salinity (S) and thickness of oil film on the water surface is described. This method is based on the analysis of spectral shape changes of water<sub>1</sub> Raman scattering band 3100...3700 cm<sup>-1</sup>. Two algorithms of sea water T&S evaluation are proposed for the case when the dispersion of hydrooptical features is not negligible (like during natural remote sensing). The Argon ion laser ( $\lambda_{exc}=488$  nm) has been used for excitation of Raman scattering in water and optical multichannel analyzer has been used for spectra detection.

KEY WORDS: Remote Sensing, Raman Scattering, Water, Oil Pollutions, Temperature and Salinity

1. INTRODUCTION

The Raman backscattered signal from water molecules can be used in remote fluorescent techniques as an internal standard to minimize the effects of laser beam penetration into the water column. The resulting intensity ratios are independent on the laser output power and the altitude of the fluorosensor, etc.

The other usage of water Raman stretching band is the measuring some characteristics as temperature and salinity of sea water, dispersion of attenuation coefficient, thickness of oil film on water surface.

The method of the remote measurement of the sea water temperature (T) is based on the dependence of the water Raman scattering band on T (Chang C.H. et al., 1974; Leonard D.A., Caputo B., 1983).

In our laboratory the method of simultaneous determination of two water characteristics - temperature and salinity (T&S) - using water Raman stretching band 3100...3700 cm<sup>-1</sup> has been elaborated in 1983 (Bekkiev A.Yu. et al., 1983). Though dependence of water Raman spectra on T&S changes is weak, the use of least squares method or mathematical "reduction method" has allowed to achieve good results of T&S

evaluation both in laboratory experiments and in remote sensing of sea water surface (Baulin E.V. et al, 1988).

In case of remote sounding of sea water deep layer the presence of dispersion  $d\varepsilon/d\lambda$  of scattering light attenuation coefficient leads to big distortions of detected spectral shape and thus to essential errors in T&S diagnostics. Our estimations show that errors resulting from dispersion  $d\varepsilon/d\lambda$  for the typical values of hydrooptical parameters ( $\varepsilon = 0.1...0.2$  m<sup>-1</sup>,  $d\varepsilon/d\lambda = 2 \cdot 10^{-3}$  m<sup>-1</sup>/nm) are equal: 1 °C & 1% for each 1m of depth in sounding thin deep layer; 5...10 °C & 5...10% in sensing of semi-infinite sea water (Patsayeva S.V. et al, 1990).

In this communication we observe the case when the dispersion of hydrooptical features is not negligible (like in natural remote sensing) and spectral function  $\varepsilon(\lambda)$  is unknown.

2. LEAST SQUARES METHOD OF SEAWATER TEMPERATURE AND SALINITY MEASUREMENT

In our problem  $I_i$  ( $i=1...500$ ) are intensity values of detected water Raman stretching band in 500 spectral channels of the optical multichannel analyzer (OMA). According to our experimental research (Baulin E.V. et al, 1988) the intensity of water Raman spectrum normalized to unit area is linear regression from T and S for each spectral channel i :

$$I_i = (\alpha_i \cdot T + \beta_i \cdot S + \gamma_i) \quad (1).$$

The coefficients of measurement model (1)  $\alpha_i$ ,  $\beta_i$ ,  $\gamma_i$  can be calculated from calibration experimental spectra for seawater samples with different temperatures and salinities.

For the spectrum of sea water with unknown T&S  $\{I_i\}$  we can use common least squares method minimizing next sum:

$$\sum_{i=1}^{500} \{I_i^* - (\alpha_i \cdot T + \beta_i \cdot S + \gamma_i)\}^2 \quad (2).$$

Then we have two linear equations with two unknown parameters T and S:

So we can calculate T and S. Large spectral information (500 spectral channels in our case) increases the accuracy of T and S determination.

$$\begin{cases} T \cdot \sum_{i=1}^{500} \alpha_i^2 + S \sum_{i=1}^{500} \alpha_i \cdot \beta_i + \sum_{i=1}^{500} (\alpha_i \cdot \gamma_i - \alpha_i \cdot I_i^*) = 0 \\ T \cdot \sum_{i=1}^{500} \alpha_i \cdot \beta_i + S \sum_{i=1}^{500} \beta_i^2 + \sum_{i=1}^{500} (\beta_i \cdot \gamma_i - \beta_i \cdot I_i^*) = 0 \end{cases} \quad (3)$$

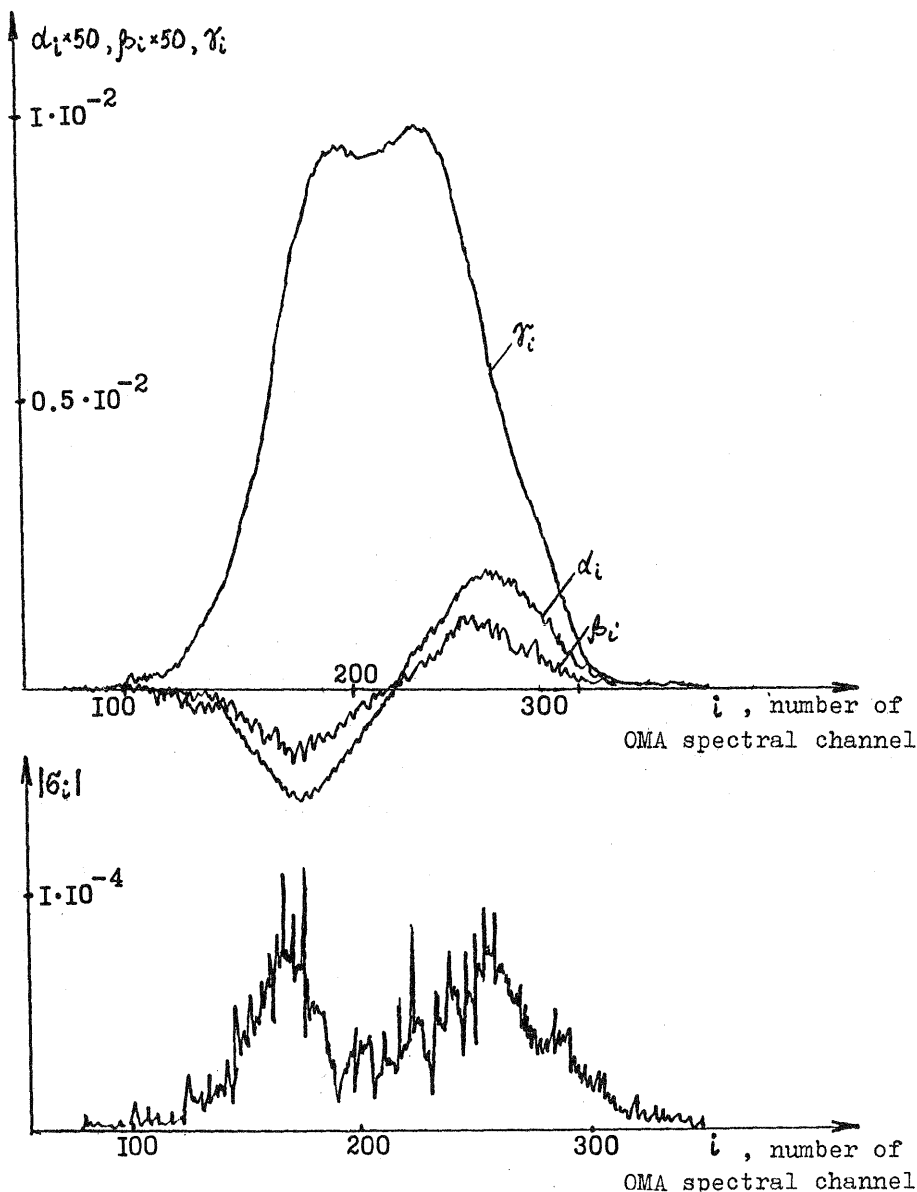


Fig.1. Coefficients of measuring model for water Raman spectrum. Water Raman spectra were detected under laboratory conditions by optical multichannel analyzer with excitation by Argon laser (488 nm).

### 3. METHOD OF MINIMAL SPECTRAL DISTORTION

Raman scattering spectrum from thin deep-water layer differs from this one from subsurface sea water layer because of presence of exponential factor  $\exp(-(\epsilon(\lambda_0) + \epsilon(\lambda_1))z)$ , where  $\lambda_0$  and  $\lambda_1$  are excitation and detection wavelengths,  $z$  is the depth of sensing layer. We use the linear approximation of  $\epsilon(\lambda_i)$  near the central wavelength  $\lambda_R$ :

$\epsilon(\lambda_i) = \epsilon(\lambda_R) + (d\epsilon/d\lambda)\Delta\lambda_i$ . Define  $\kappa = (d\epsilon/d\lambda)_{\lambda=\lambda_R}$ ;  $\Delta\lambda_i = \lambda_i - \lambda_R = i$  (number of spectral channel of detector). Also we use approximate equality  $\exp(-\kappa \cdot i) \approx 1 - \kappa \cdot i$ . For natural sea water the value  $d\epsilon/d\lambda \sim 10^{-3} \text{ m}^{-1}$  so this approximation is valid while depth  $z < 100\text{m}$ . If spectrum is area normalized all wavelength independent factors disappear and the measurement model becomes:

$$I_i(\kappa) = (1-\kappa \cdot i)(\alpha_i \cdot T + \beta_i \cdot S + \gamma_i) \quad (4).$$

Measurement model coefficients  $\alpha_i$ ,  $\beta_i$ ,  $\gamma_i$  are the same in the model (1) and can be calculated from test experimental spectra for seawater sample or surface water layer. So for each value  $\kappa$  we can correct the water Raman spectrum and evaluate  $T(\kappa)$  and  $S(\kappa)$  using standard least squares method. These  $T(\kappa)$  and  $S(\kappa)$  will be truth if  $\kappa$  is equal to real  $\kappa_0$ .

Let's define parameter of spectral distortion:

$$D(\kappa) = \sum_i \{I_i - (1-\kappa \cdot i)(\alpha_i \cdot T(\kappa) + \beta_i \cdot S(\kappa) + \gamma_i)\}^2 / \sigma_i^2 \quad (5),$$

where  $\sigma_i^2$  is spectral intensity dispersion for  $i$  spectral channel. For any  $\kappa$  we can calculate  $D(\kappa)$ .

To estimate  $T$  and  $S$  in the case of measurement model with unknown  $\kappa = (d\varepsilon/d\lambda)_{\lambda=\lambda_R} z$  we use the next algorithm.

1. We calculate the values of spectral distortion  $D(\kappa)$  for different parameters  $\kappa$ .
2. We select parameter  $\kappa$  so that  $D(\kappa)$  be minimal value.
3. For this  $\kappa$  we estimate T&S using standard method.

This algorithm has been applied for T&S evaluation (Patsayeva S.V., Fadeev V.V., 1991) from experimental Raman scattering spectra (detected under laboratory conditions). It has been shown that additional error caused by unknown coefficient  $\kappa = (d\varepsilon/d\lambda)z$  is less than 0.2 °C & 0.2‰.

#### 4 TWO EXCITATION WAVELENGTHS METHOD

In the second algorithm (Patsayeva S.V., Fadeev V.V., 1991) two water Raman spectra are detected using two excitation wavelengths, so both Raman spectra are partially overlapped. This algorithm was tested in our laboratory using two YAG-lasers with second harmonics ( $\lambda_1=532$  nm,  $\lambda_2=538$  nm).

The spectral intensity for each spectrum is described by measurement model (2) with different coefficients of regression  $\alpha$ ,  $\beta$ ,  $\gamma$ , but the same factor  $(1-\kappa \cdot i)$ . The spectral contour which is a ratio of two Raman spectra depends on T&S but not on  $d\varepsilon/d\lambda$ . Using linear approximation of this dependence on T&S and common least squares method of Raman spectra handling we can evaluate T&S. This algorithm is principally similar to "polarized spectra" technique (Leonard D.A., Caputo B., 1983), but more comfortable in practice.

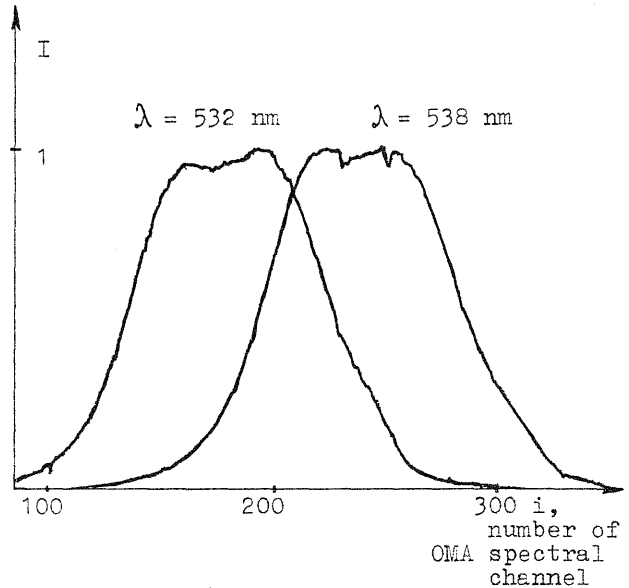


Fig.2. Two water Raman spectra detected using two excitation wavelengths ( $\lambda=532$ ,  $538$  nm).

Thus, described algorithms allow us to evaluate sea water temperature and salinity from Raman scattering spectra distorted by attenuation coefficient dispersion and when spectral function  $\varepsilon(\lambda)$  is not a priori known.

#### 5. OIL FILM THICKNESS MEASUREMENT USING RAMAN SCATTERING

The importance of oil pollutions (OP) monitoring is assuredly increasing in our days because of the tragedy in the Persian Gulf and few accidents with oil tankers occurred recently.

The fluorescent technique with laser UV excitation for remote sensing of oil films on water surface is very common (Visser H., 1979; Hoge F.E., 1983; Hengsterman T., Reuter R., 1990). But the main problem is the spectral interference of fluorescence of natural dissolved organic matter (yellow substance), OP in water column and oil film.

Some investigators (Kung R.T.V., Itzkan I., 1976; Hoge F.E., Swift R.N., 1980; Hengsterman T., Reuter R., 1990) for oil thickness measurement use depression of water Raman intensity by oil film. This technique requires knowing the extinction coefficient of oil film ( $\varepsilon_0 + \varepsilon_r$ ) at excitation and Raman scattering wavelengths or the identification of oil product. Some problems arising from this technique are: measuring signal is dependent on such experimental conditions as laser power variations, laser beam penetration into the water column, etc.

In this work we offer another technique for oil film thickness measurement using contour analysis of water Raman spectra.

The Raman stretching band distorts in shape due to presence of dispersion  $d\varepsilon_{op}/d\lambda$  of attenuation coefficient of oil film on water surface. On the fig. 3 there are shown simulated Raman spectra of water distorted by  $d\varepsilon_{op}/d\lambda = 0.0025 \text{ nm}^{-1}\text{mkm}^{-1}$  for different thickness of oil film  $d = 2 \dots 10 \text{ mkm}$  (upper curves) and differences between simulated spectra and original undistorted Raman spectrum of water (lower curves). All Raman spectra are normalized to unit area.

This value of dispersion corresponds with minimal dispersion from experimental results on absorption for different type of oils in spectral region 337-407 nm (Camagni P., et al, 1991). For heavy oils dispersion and therefore Raman spectrum distortion is much bigger.

Our model calculations show that Raman intensity  $I_i$  in  $i$  spectral channel of optical multichannel analyzer is practically linear from  $d$  up to 50 mkm (with dispersion value  $d\varepsilon_{op}/d\lambda = 0.0025 \text{ nm}^{-1}\text{mkm}^{-1}$ ).

The measuring model is described by the formula (4) with parameter  $\kappa = (d\varepsilon_{op}/d\lambda)d$ . If temperature and salinity of sea water are known or constant, the measuring model is described by :

$$I_i(d) = (1-\kappa i)(\alpha_i T + \beta_i S + \gamma_i) = A_i + B_i d \quad (6).$$

Coefficient  $B_i$  depends on dispersion  $d\varepsilon_{op}/d\lambda$ . For  $d$  calculation we can use any of the above-mentioned methods for temperature measuring from water Raman spectrum: "two-color method", "polarized spectra technique", "least squares", "reduction method".

Thus, detecting spectral distortions of Raman scattering spectrum from water with oil film, we can estimate a thickness of oil film (if the value of dispersion  $d\varepsilon_{op}/d\lambda$  is known). Let's mark that this technique operates with Raman spectra, normalized to unit area. So measuring process does not depend on laser power, experimental conditions, laser beam penetration into the water column, etc.

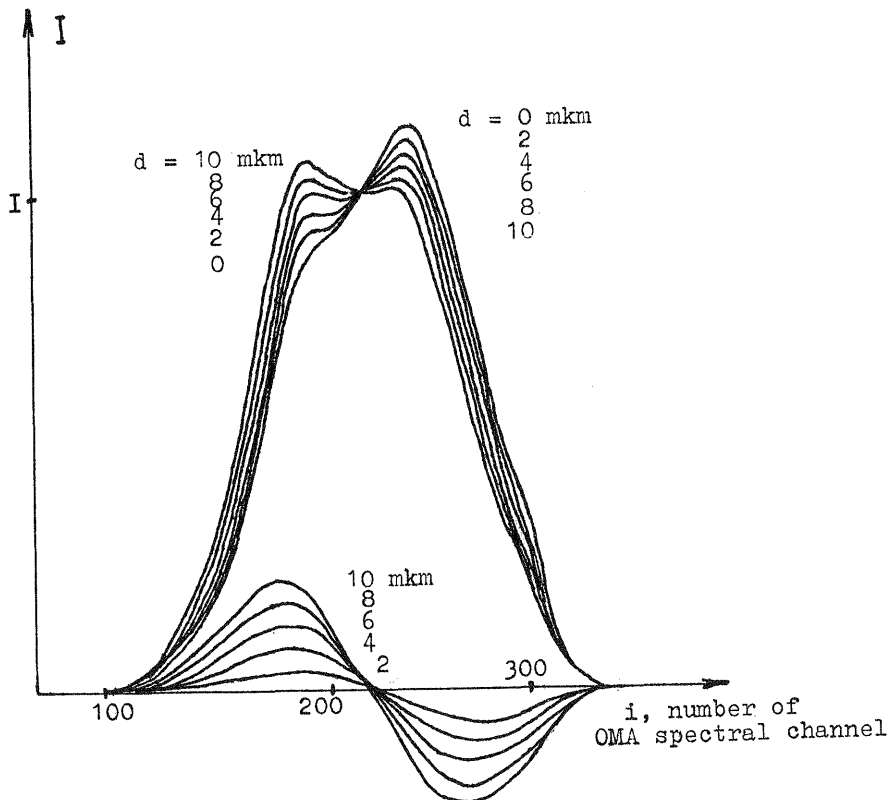


Fig.3. Simulated water Raman spectra distorted by  $d\varepsilon_{op}/d\lambda = 0.0025 \text{ nm}^{-1}\text{mkm}^{-1}$  for different thickness of oil film  $d = 2 \dots 10 \text{ mkm}$  (upper curves) and differences between simulated spectra and original undistorted Raman spectrum of water (lower curves). All Raman spectra are normalized to unit area.

## 6. CONCLUSION

Thus, in this work it has been shown that contour analysis of laser induced water Raman spectra provides us with measurement of thickness of oil film on water surface, temperature and salinity of seawater.

Temperature and salinity can be measured also when dispersion of attenuation coefficient for light in seawater is unknown.

This technique operates with water Raman stretching band normalized to unit area. That means that detecting intensities do not depend on laser output power and experimental conditions during remote sensing.

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