

A Portable Surface Enhanced Raman Spectroscopy (SERS) Sensor System Applied for Seawater and Sediment Investigations on an Arctic Sea-Trial*

Anna Kolomijeca and Heinz-Detlef Kronfeldt

Institute of Optics and Atomic Physics, Technical University Berlin (TUB), Berlin, Germany

Yong-Hyok Kwon

Institute of Optics and Atomic Physics, Technical University Berlin (TUB), Berlin, Germany

Institute of Lasers, Academy of Sciences, Pyongyang, DPR Korea

In this paper we introduce, for the first time, a portable on-board Surface Enhanced Raman Spectroscopy (SERS) Sensor System on an Arctic sea-trial, applying a 671 nm microsystem laser diode. During a three-week cruise on the James Clark Ross (JCR) research vessel in August 2011, the measurements of Arctic water column and sediments were taken around 78° N and 10° E. Raman and SERS spectra of Arctic surface and sediment water are presented as well as the results of short-time and long-time substrate stability tests. Spiking experiments with PAHs (anthracene, fluorethene and pyrene) in different concentrations were also carried out.

INTRODUCTION

The International Panel on Climate Change (IPCC, 2007) has identified the Arctic as the area of the planet most affected by climatic changes. Barrie et al. (1992), Hallanger (2010), Sapota et al. (2009) and other studies show that the Arctic is home to several toxic organic pollutants.

Polycyclic aromatic hydrocarbons (PAHs) are dangerous environmental pollutants formed during incomplete combustion of coal, oil and gas (Lohmann et al., 2009). PAHs are dissolved in seawater with low concentrations in the range of nM or less and their concentration profiles are changing temporally and spatially (Witt, 2002). These pollutants were found in the Arctic area in 2005 (sampling date), in surface sediments from lakes (2 µM) and Fjords (180 nM) around the Spitsbergen area (Sapota et al., 2009).

Most pollutants around Svalbard come as atmospheric deposits from the local mining industries and coal-fired power stations in the Isefjord (Rose et al., 2004). The pollutants are transferred to the Arctic through the atmosphere, ocean currents, and rivers (Barrie et al., 1992; Fellin et al., 1996). The atmospheric transportation of pollutants mostly comes from industrially developed countries in Europe and North America (Pacyna and Ottar, 1985; Barrie, 1986; Beine et al., 1996; Burkow and Kallenborn, 2000).

Typical chemical methods for water/sediment analysis are complex and time consuming. The aim of our group is to develop a fast-response, in-situ sensor, for easy handling and rapid analysis. Several studies were made by Hester et al. (2006), Peron et al. (2010), Breier et al. (2010) and White (2008), using Raman spectroscopic techniques for identification of different components in the sea water. This type of vibrational spectroscopy is noninvasive and provides spectral “fingerprints” of the molecules. The

major disadvantage, however, is that Raman scattering is very weak. Therefore, for the detection of molecules in low concentrations, the sensitivity of this technique must be increased by several orders of magnitude. This can be achieved by applying surface-enhanced Raman scattering developed by Fleischmann et al. (1974).

In this paper we introduce a portable Raman (SERS) set-up with a 671 nm microsystem laser diode tested in real field conditions. The main delivery of our project is to carry out pilot-studies of the Raman sensor in “extreme” real-field conditions as an intermediate step between the construction of a sea-going instrument and laboratory experiments. For this purpose, surface water and sediment samples were examined in twenty locations in three weeks (August 2nd–21st, 2011), in the area of 78° N and 10° E onboard the James Clark Ross research vessel.

All water samples were analyzed with Ag.DMCX:MTEOS substrate (Kwon et al., 2011a; Kwon et al., 2011b).

MATERIALS AND METHODS

Preparation of SERS Substrate

To prepare Ag.DMCX:MTEOS, substrate quartz slides with a thickness of 1 mm and diameter of 10 mm are cleaned using piranha solution, which is heated at 70°C for 30 minutes, rinsed with methanol several times and stored in methanol until use. To prepare the sol-gel film embedding, the silver colloid functionalized with DMCX, 17.4 mg of silver nitrate are dissolved in 60 µl of pH 0.6 H₂O. The pH value is controlled by HNO₃. To this solution, 149 µl of ethanol, containing DMCX with a concentration of 1 mM and 163 µl of methyltriethoxy-silane (MTEOS), are added to form the sol solution. The mixture is stirred with a stir bar and after 5 minutes every quartz section is spin-coated with this solution at 3000 rpm for 10 seconds. The substrates are heated for 17 hours at 70°C. After that, silver nitrate in the sol-gel film is thermally reduced by heating to 230°C for 2 hours, forming the silver colloid functionalized with DMCX in MTEOS derived sol-gel film (Kwon et al., 2011a; Kwon et al., 2011b). Before measurement, the prepared SERS substrates are stored in distilled water. For every measurement, a new substrate is used, unless for stability tests.

*The best student paper presented at the Twenty-second (2012) International Offshore and Polar Engineering Conference, Rhodes, Greece, June 17–22, 2012.

Received July 6, 2012; revised manuscript received by the editors March 11, 2013. The original version (prior to the final revised manuscript) was presented at the 22nd International Offshore and Polar Engineering Conference (ISOPE-2012), Rhodes, Greece, June 17–22, 2012.

KEY WORDS: Raman sensor, SERS, JCR arctic, Portable Raman system, PAHs.