

# Application of Silver Halide Paper for Surface-Enhanced Raman Studies of Organic Compounds

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## Introduction

The establishment of Infrared and Raman spectroscopy in chemical analysis offers the possibility to identify organic compounds on the basis of vibrational bands being characteristic of certain functional groups. Due to the low sensitivity of conventional Raman spectroscopy this technique plays a subordinate role in analysis [1]. With the discovery of Surface-Enhanced Raman Scattering (SERS) by Fleischmann et al. in 1974 [2], Raman spectroscopy became a potential tool for quantitative analysis.

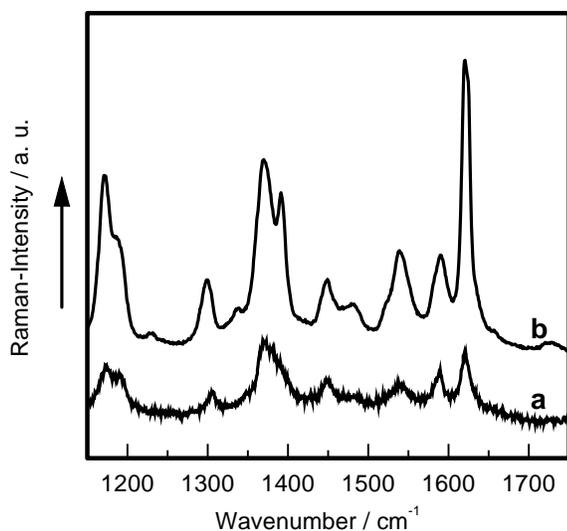


Figure 1: (a) Raman spectrum of crystal violet ( $c = 0.1 M$ ), (b) SERS spectrum of crystal violet ( $c = 1 \times 10^{-5} M$ ). All experimental parameters were kept constant ( $\lambda_{exc} = 514.5 \text{ nm}$ ,  $P = 25 \text{ mW}$ , integration time 5 s).

After the adsorption of the substance on a properly structured, coin metal surface the intensity of the light scattered by an adsorbed molecule is between 6 and 11 orders of magnitudes higher compared with a molecule not adsorbed at the surface. Usual SERS active surfaces are, for

example, metal colloids and electrochemically or chemically roughened electrodes. The reproducible preparation of supports of this kind is, however, very difficult as was discovered during previous work. In Fig. 1 the SERS effect is demonstrated for crystal violet adsorbed at the surface of colloidal silver.

Silver halide based photographic material is also known as a SERS active surface [3] but no statements about the reproducibility of SERS spectra recorded with photographic materials are reported.

In this paper we will show that reproducible SERS spectroscopy with photo paper can be reached when the experimental parameters of both the photographic process and the SERS measurements are kept constant. The application of this kind of light sensitive material as a SERS active substrate to investigate adsorption phenomena is described in the following.

## Preparation of the Photographic Material

For our investigations commercial photographic paper for black and white prints was used.

After illumination with the diffuse light of an enlarger the photographic paper was developed in a commercial black and white developer.

Long illumination and developing times were chosen to convert most of the  $\text{Ag}^+$  into  $\text{Ag}^0$ . Usually no hardening with thiosulfate was carried out. The 514.5 nm and the 457.9 nm lines of an  $\text{Ar}^+$ -laser (Spectra Physics) were used for generating the scattered light. In a  $180^\circ$  backscattering arrangement a computer-controlled diode array camera (IRY 700, Spectroscopy Instruments) was placed at the output plane of a double spectrograph (DHR 320, Jobin Yvon) to take the SERS and Raman spectra.

Trace (a) in Fig. 2 represents the SERS spectrum of oxazine 170 on developed but unhardened photo paper. The effect of the hardening process on the SERS signal, carried out with commercially available  $\text{S}_2\text{O}_3^{2-}$ -based hardener, can be seen in Fig. 2 trace (c).

The fact that the hardening of the paper leads to a complete disappearance of the SERS signal may have two reasons; either the SERS activity of the unhardened paper is the result of the spontaneous formation of silver specks

during the illumination of the sample by the probing laser or the loss of SERS activity is the consequence of a change of surface properties caused by the developer. To exclude the first possibility, a developed and CN<sup>-</sup>-hardened paper was used for SERS measurements to make sure that all residual silver halide had been removed (the hardener consisted of a 0.1 M aqueous solution of KCN, exposure time was 10 s). The enhancement of the CN<sup>-</sup>-hardened paper is comparable to the enhancement of the unhardened paper (trace b, Fig.2). Therefore it can be concluded that the fixing leads to a coverage of the surface by Ag<sub>2</sub>S [4] which destroys the plasmon resonance condition of the silver particles being responsible for the SERS effect.

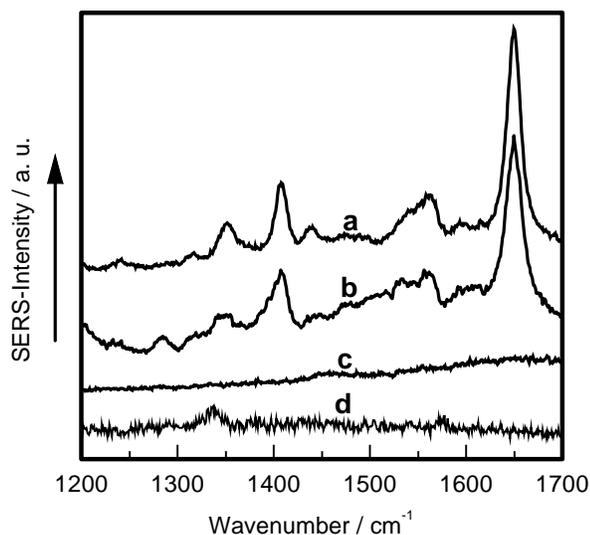


Figure 2: SERS-spectra of oxazine 170 ( $c = 1 \times 10^{-5} M$ ) on (a) developed but unhardened, (b) developed and CN<sup>-</sup>-hardened and (c) developed and S<sub>2</sub>O<sub>3</sub><sup>2-</sup>-hardened photo paper. (d) is the normal Raman signal of the dye solution (the weak bands at 1337 cm<sup>-1</sup> and 1580 cm<sup>-1</sup> originate from the polyacryl cuvettes,  $\lambda_{exc} = 514.5 nm$ ,  $P = 10 mW$ ).

SERS spectra taken with untreated photo paper (no illumination and no development) demonstrate that there is SERS activity which is dependent on the exposure time by the probing laser (not shown). That in trace (a) and (b) of Fig. 2 the SERS intensities are comparable to each other provides evidence that nearly no undeveloped silver halide remains in the case of the unhardened paper.

### Application of Photographic Paper for Analytical Purposes

Among other things, the application of SERS spectroscopy as a tool for quantitative analysis is limited by undesirable properties of the different kinds of surfaces (e.g. coagulation of colloids after mixing them with a substance [5] or poor reproducibility of roughened electrode surfaces).

With the use of photographic paper many of those problems can be avoided. Nowadays commercially available photopaper is produced in a high and uniform quality thus

the preparation of the SERS active surface is reproducible too, if the conditions of preparation are controlled exactly. Consequently, the recorded SERS intensity is reproducible within about 5%, even if samples are used which have been prepared independently according to the same recipe (Fig. 3).

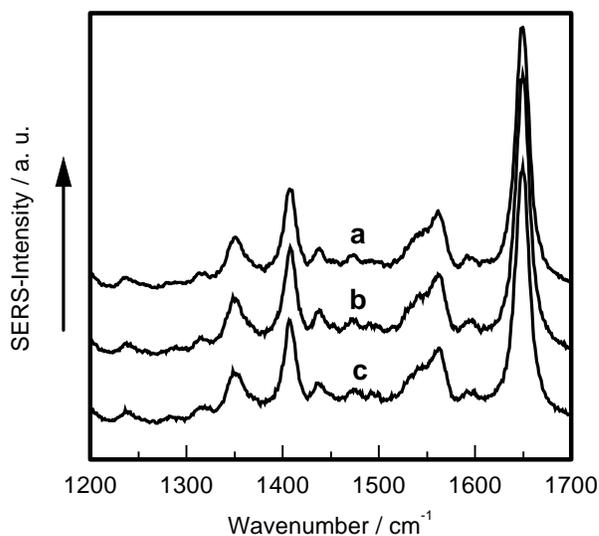


Figure 3: Demonstration of signal reproducibility. Spectra are recorded with different samples of developed and unhardened photo paper which were treated in the same manner. Dye is oxazine 170 ( $c = 1 \times 10^{-5} M$ ,  $\lambda_{exc} = 514.5 nm$ ,  $P = 10 mW$ ).

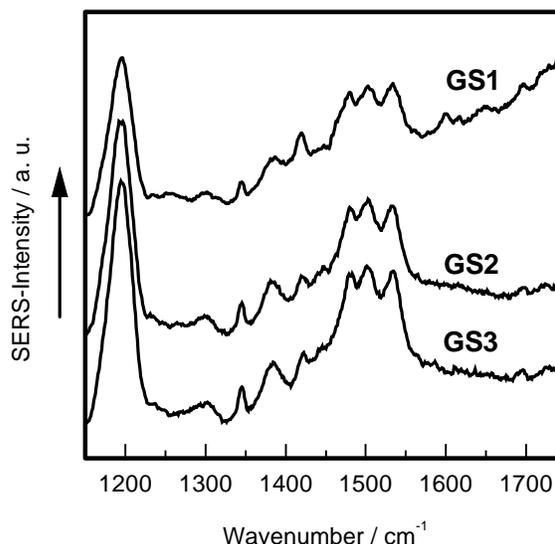


Figure 4: SERS spectra of aqueous solutions of different green sensitizers ( $c = 1 \times 10^{-5} M$ ) recorded with developed but unhardened photo paper ( $\lambda_{exc} = 457.9 nm$ ,  $P = 50 mW$ ).

One of the main prerequisites for the SERS effect is the adsorption of the molecules at the surface. Substances which

contain sulfur and/or nitrogen within their structural formulae are predestined for adsorption at silver surfaces [6]. In Fig. 4, the SERS spectra of several green sensitizers, applied in photographic materials recorded on photo paper are shown (solutions with the same sensitizer concentrations yield no detectable Raman signal). The comparison of SERS-spectra of the same sensitizers recorded with colloids [7] show some differences in the intensity of several bands. This could be in the part due to different additives which are in the photographic paper and the colloidal solution respectively.

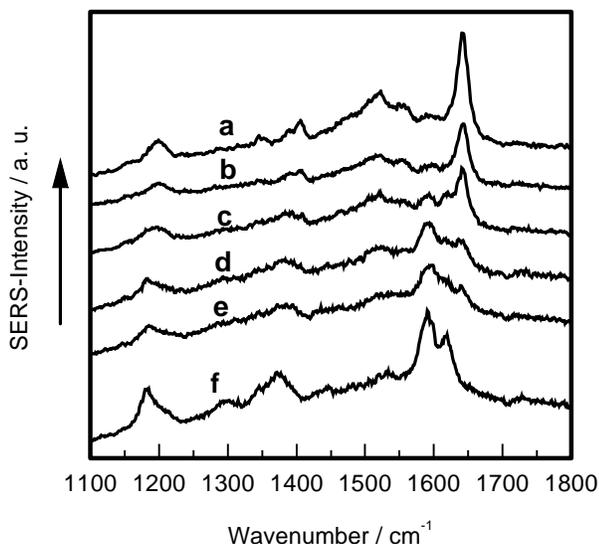
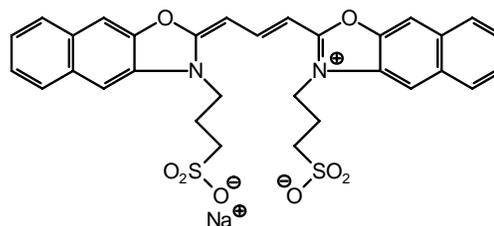


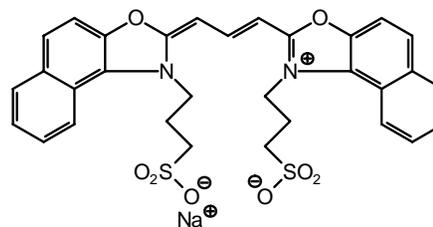
Fig. 5: SERS spectra of  $1 \times 10^{-5} M$  aqueous solutions of oxazine 170 (a) and crystal violet (f); (b) - (e) show the time dependent changes of the spectrum after adding crystal violet to the oxazine 170 solution; the time delay between consecutive spectra is 5s (b), 1 min (c), 5 min (d) and 10 min (e). The spectra were taken with developed but unhardened photo paper, the concentration of both dyes were  $1 \times 10^{-5} M$  in all cases ( $\lambda_{exc} = 457.9 \text{ nm}$ ,  $P = 50 \text{ mW}$ ).

It is obvious that all three structural isomers (see formulae below) are able to diffuse through the gelatin layer and adsorb at the surface. In spite of the structural similarity of these sensitizers the respective SERS spectra are characteristic of each substance. Although many substances have the ability to adsorb at silver, their heats of adsorption differ considerably. Therefore, a competition for free adsorption sites at the surface will occur if the sample contains several components [8]. This competitive adsorption can be used to estimate relative adsorption heats of different molecules. As an example, Fig. 5 shows the time dependent displacement of oxazine 170 on the silver grains by crystal violet. The characteristic  $1647 \text{ cm}^{-1}$ -band of oxazine 170 disappears whereas the bands at  $1590 \text{ cm}^{-1}$  and  $1620 \text{ cm}^{-1}$  of crystal violet become more intensive. Similar investigations with oxazine 170 and water blue prove that oxazine 170 is able to substitute water blue at the developed silver surface (not shown). As a result it can be stated that the values of the heats of adsorption increase in the sequence water blue, oxazine 170, crystal violet.

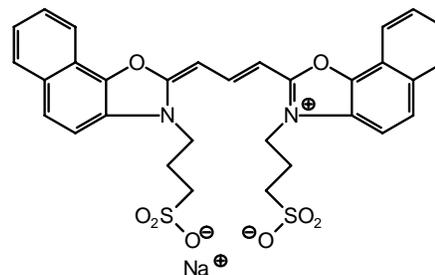
## List of Substances used for this Paper



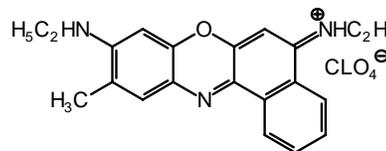
green sensitizer 1 (GS1)



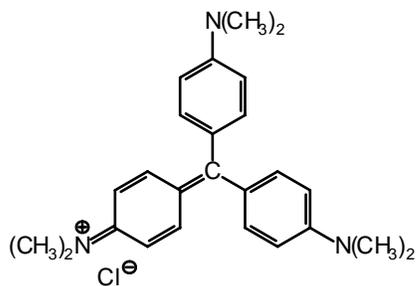
green sensitizer 2 (GS2)



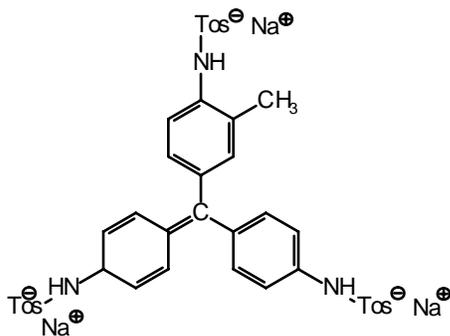
green sensitizer 3 (GS3)



oxazine 170



crystal violet



water blue

### Summary and Conclusion

The application of photographic paper for SERS spectroscopy is one way to overcome several disadvantages of other kinds of surfaces. If the preparation of the photographic paper is performed according to a well defined exposure and development procedure, then the signal

intensity is reproducible to a few percent as long as all other experimental parameters are kept constant. We are convinced therefore that the SERS active substrates prepared from commercially available photographic materials are suited for qualitative and quantitative determination of organic compounds, especially if calibration of the signal intensity can be made with solutions of known concentration.

### Acknowledgement

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### Literature

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