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Multiple SERS Detection of Phenol Derivatives in Tap Water[†]

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Abstract: Phenol and some of its derivatives are products of the petrochemical industry. These compounds are characterized by their exceptional ability to persist in the media and reach both food and water used by human beings. The consumption of these compounds has harmful effects on the health producing both acute and chronic, among the most prominent damages are teratogenicity, mutagenicity and carcinogenicity. Compounds like phenol, ortho-cresol, and 1-napthol are listed by agencies like the EPA. The aim of this work was the development of a rapid method for the detection of these compounds simultaneously in water samples. The method was based on the colorimetric reaction between the phenol derivatives and the Gibbs reagent to form indophenolates and using increased surface Raman spectroscopy together with statistical methods, the SERS spectra of the different spectra were got, which were then analyzed. The developed method allows at least to equalize the detection limits of the colorimetric method through UV-VIS spectroscopy and to discriminate among these three mixed phenols in at least binary aqueous samples. The major advantage of the method is the possibility of discriminating between phenol spectra quickly and easily.

Keywords: SERS; phenol derivatives; Raman Spectra; water samples; Gibbs reactive

1. Introduction

Phenol and its derivatives are compounds generally produced by the petrochemical industry, although to a lesser extent they can be produced naturally. In addition, they are also part of a multitude of pesticides These compounds have one or more phenolic rings and are widely persistent in media. They produce both acute and long-term effects, among the long-term effects are: carcinogenicity, mutagenicity, teratogenicity and others, therefore control agencies such as the EPA have established limits for them [1]. The reference method for the determination of total phenols in water is based on the spectrophotometric measurement of the product of the reaction of total phenols with 4-aminoantipyrine [2,3].The aim of this method is to develop a rapid system for the detection of phenol and some of its derivatives in water samples. This method is based on the comparison of the SERS spectra of the different indophenolates formed after the reaction in a basic medium between the Gibbs reagent and phenol and its derivatives [4–6]. The analysis by UV-VIS allows the quantification of total phenols present in the water sample, however, it is not possible to distinguish between them. For this reason, the SERS spectra of the reaction products have been obtained and have been analyzed using principal component analysis to look for differences between the different concentrations of the same compound and between different compounds.

2. Material and Methods

2.1. Materials

Phenol 99%, ortho-cresol 99% and 1-naphtol 99% were purchased from Sigma-Aldrich, 2,6-dichloroquinone-4-chloroimide (dbqc) 97% was purchased from Sigma-Aldrich. Milli-Q water was employed in the synthesis of nanoparticles. The SERS substrate was homemade using layer-by-layer deposition of 60 nm Au@nanospheres produced by the method related by Bastús et al., (2011) [7], into a piece of glass. The characterization of the nanoparticles was carried out using a JEOL JEM 1010 Transmission Electron Microscope (TEM). UV-VIS spectra were recorded using a 8543 Agilent spectrophotometer and SERS spectra were recorded using and Renishaw InVia Reflex System.

2.2. Methods

SERS Substrates Synthesis

Following Bastús et al., (2011) 60 nm gold nanospheres were growth. These nanospheres were deposited in a glass substrate using layer-by-layer method. Getting a substrate that allows us to perform a great enhanced on the signal (Figure 1).

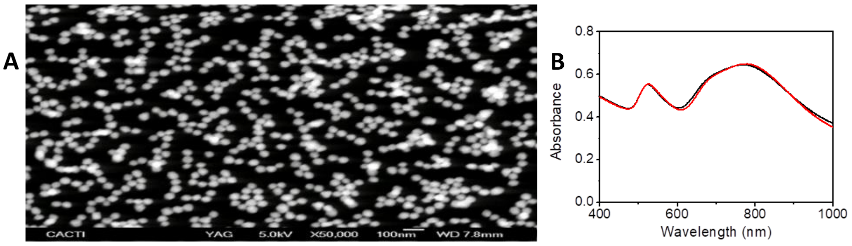

Figure 1. (**A**) TEM Image of the SERS substrate (**B**) UV-VIS spectra of the substrate.

2.3. Experiment

The experiment is based on the reaction between phenol or a non-parasubstituted phenol derivative in basic medium, to form and indophenolate. This indophenolate (Figure 2) is a green coulored compound with an absorption band around 600 nm (Figure 3). The concentration of the reactive of Gibbs employed in the experiment is always constant at 50 µM

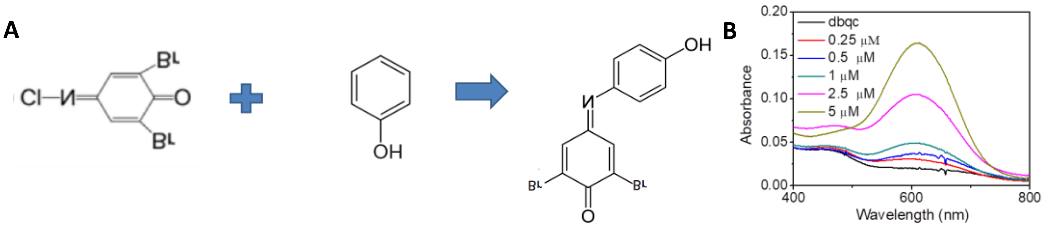

Figure 2. (**A**) Reaction between phenol and Gibbs reactive in a basic medium to form and indophenolate. (**B**) UV-VIS spectra of the result of the reaction between Gibbs reactive and a phenolic compound.

The resulting indophenolates have an absorption band around 600 nm and it is not possible to distinguish between the phenol and the phenol derivatives, for this the SERS experiment is performed. The SERS spectra were performed putting a drop of the resulting indophenolate in a SERS substrate, and measuring the spectra using a Renishaw Invia Reflex System, a 633 nm laser line was employed due to the possibility of act in resonance conditions with the 600 nm absorption band of the indophenolates.

2.4.Data

The obtained spectra were statistical analysed using R, PCA was performed to quantify and distinguish between phenols. All the data represented in the graphs are the average of at least 16 points of measurement. The regression of the SERS spectra in the phenol's case was performed using a Hill-Langmuir regression.

3. Results

The first experiment was the verification of the detection and quantification of the phenolic compounds separately. The detection limits of the spectrometric method were found to equalize and sometimes even improve. Quantification was carried out for the three phenols, describing the same in the lower figure for the case of phenol (Figure 3)

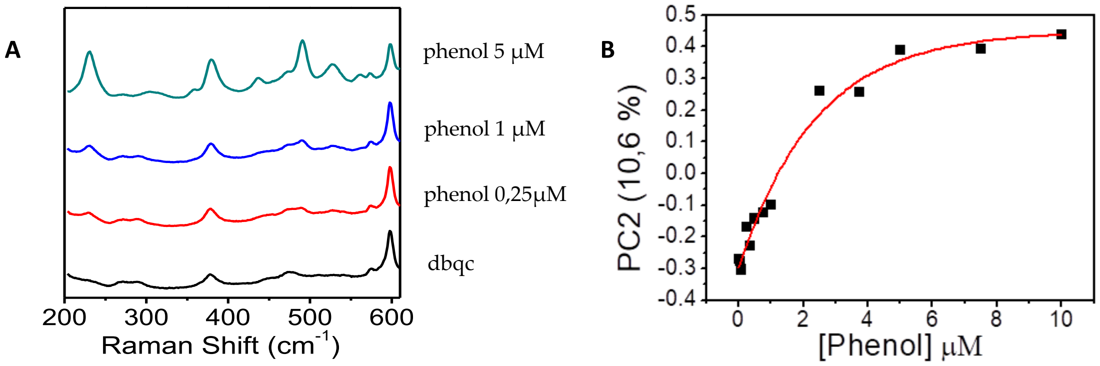

Figure 3. (**A**). Representation of the average spectra of dbqc, and the product of the reaction between the Gibbs reactive and some different concentrations of phenol. (**B**) Hil-Langmuir fitting for the concentration of phenol in the sample using PCA.

When the detection of the phenol was performed, other phenol derivatives were tried in order to try a multiplex detection, the spectra of the products of the reaction between 1-Naphthol, ortho-cresol and phenol at 5 µM concentration are represented in the figure below (Figure 4). To clearly distinguish between those SERS spectra Principal Component Analysis was performed (PCA) this technique is a powerful statistical method that looks for difference between the ratio of peaks in the spectra-(Figure 4A and 4B).

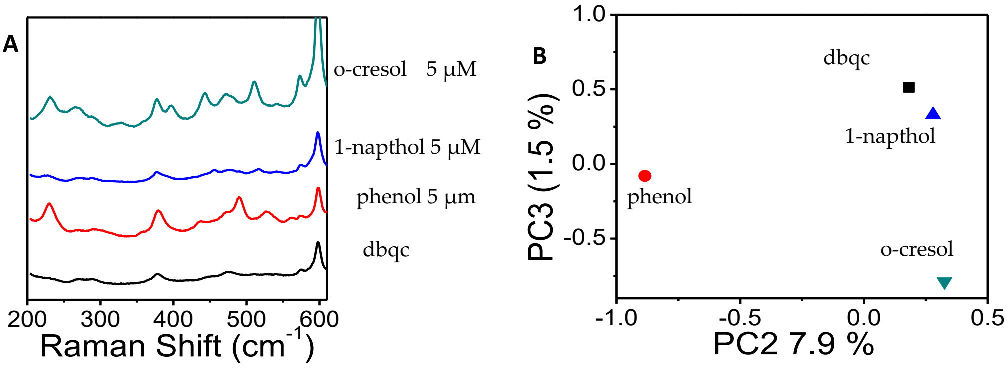

Figure 4. (**A**) Average of 16 spectra of different phenol derivatives and blank. (**B**). Representation of PCA of average spectra of phenol derivatives and blank.

To finalize the experiment, a semi-quantitative detection of the phenol and phenol derivatives was performed using binary mixtures. In this case we demonstrated that it is possible to quantify the amount of ortho-cresol and phenol in a binary mixture using our method and analyzing the data using PCA. Performing different ratios of binary mixtures between phenol derivatives allow to try a semi-quantification (Figures 5, 6, 7).

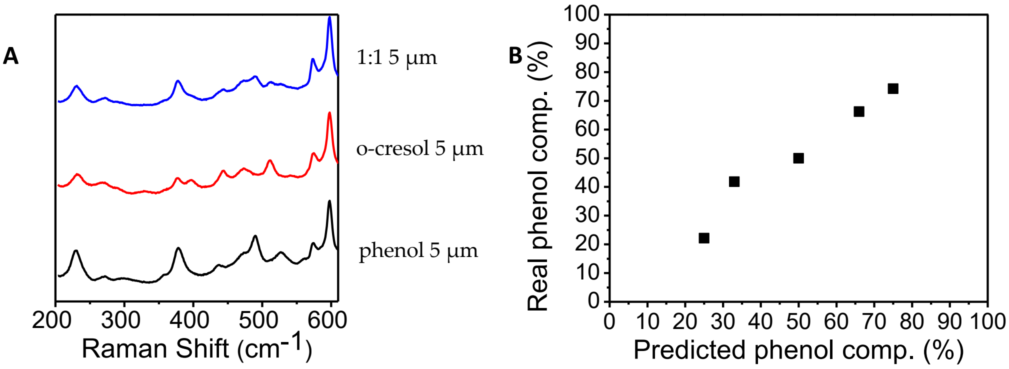

Figure 5. (**A**). Representation of the average spectra of phenol, ortho-cresol and a binary mixture between ortho-cresol and phenol 1:1 at 5 μM. (**B**) Representation of the obtained and real valued in a semiquantitative determination of binary mixtures of phenol and ortho-cresol.

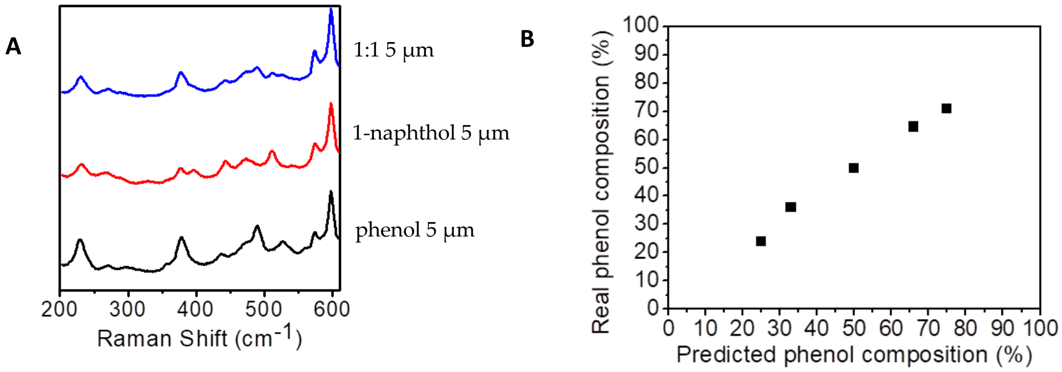

Figure 6. (A). Representation of the average spectra of phenol, 1-napthol and a binary mixture between ortho-cresol and phenol 1:1 at 5 μM. (**B**) Representation of the obtained and real valued in a semiquantitative determination of binary mixtures of phenol and ortho-cresol.

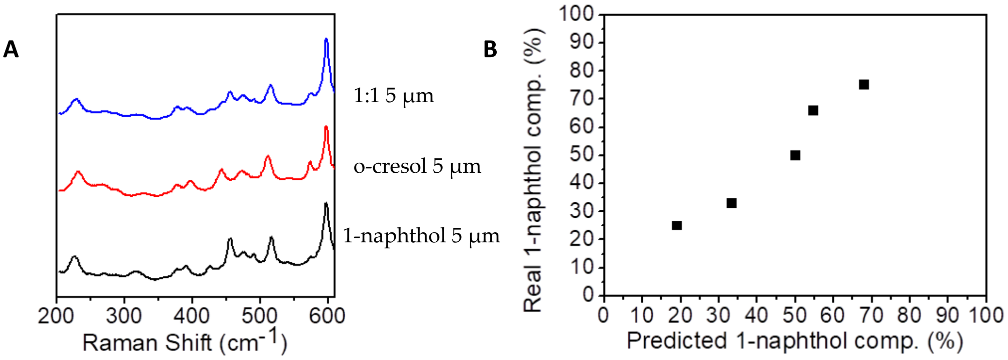

Figure 7. (**A**). Representation of the average spectra of 1-napthol, o-cresol and a binary mixture between ortho-cresol and phenol 1:1 at 5 μM. (**B**) Representation of the obtained and real valued in a semiquantitative determination of binary mixtures of phenol and ortho-cresol.

4. Discussion and Conclusion

As conclusion, it is possible to say that the method proposed could be an easy method for the detection of phenol in water. It is well recognised that SERS detection works really well in a water aqueous matrix. The detection limit that we achive it is not the better reported in the bibliography but it is enough to perform a preliminary method to detect contamination by phenols in tap water.

So, we can say that is possible to detect phenol, ortho-cresol and 1-napthol in a sample of tap water in a range between 0,25 μM and 5 μM and it is possible to differentiate and quantify at least at binary mixture level.

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References

1. US Environmental Protection Agency. *Ambient water quality criteria for pentachlorophenol*. US Environmental Protection Agency: Washington, DC, USA, 1980.
2. Acosta, C.A.; Pasquali, C.E.L.; Paniagua, G.; Garcinuño, R.M.; Hernando, P.F. Evaluation of total phenol pollution in water of San Martin Canal from Santiago del Estero, Argentina. *Environ. Pollut.* **2018**, *236*, 265–272.
3. Schmauch, L.J.; Grubb, H.M. Determination of Phenols in Waste Waters by Ultraviolet Absorption. *Anal. Chem.* **1954**, *26*, 308–311.
4. Du, B.; Su, X.; Yang, K.; Pan, L.; Liu, Q.; Gong, L.; Wang, P.; Yang, J.; He, Y. Antibody-Free Colorimetric Detection of Total Aflatoxins in Rice Based on a Simple Two-Step Chromogenic Reaction. *Anal. Chem.* **2016**, *88*, 3775–3780.
5. Josephy, P.D.; Van Damme, A. Reaction of Gibbs Reagent with Para-Substituted Phenols. *Anal. Chem.* **1984**, *56*, 813–814.
6. Svobodová, D.; Křenek, P.; Fraenkl, M.; Gasparič, J. Colour reaction of phenols with the gibbs reagent. The reaction mechanism and decomposition and stabilisation of the reagent. *Mikrochim. Acta* **1977**, *67*, 251–264.
7. Bastús, N.G.; Comenge, J.; Puntes, V. Kinetically controlled seeded growth synthesis of citrate-stabilized gold nanoparticles of up to 200 nm: Size focusing versus ostwald ripening. *Langmuir* **2011**, *27*, 11098–11105.