Analysis of benzoyl-peroxide and formaldehyde as dental allergens by FT-SPR method

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Analysis of benzoyl-peroxide and formaldehyde as dental allergens by FT-SPR method

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Abstract. In parallel with the appearance of new dental materials the number of induced allergic diseases increases. Based on this fact more sensitive detection of allergens is major importance. The Fourier-Transform Surface Plasmon Resonance (FT-SPR) is a sensitive, broadly applicable real-time method for analysing thin layers of materials on gold surfaces. FT-SPR measurement is performed at a fixed angel of incident light, and reflectivity is measured over a range of wavelength in the near infrared. In our study the formaldehyde and benzoyl-peroxide were examined as members of the most common dental allergens by FT-SPR spectroscopy. The aim of this work was the investigation of the suitability of this method for the direct detection of these materials. Different concentrations of formaldehyde and benzoyl-peroxide solutions were measured from this purpose. The individual spectra were measured for all of the solutions, and calibration curves were calculated for the materials for the possibility of the determination of an unknown concentration. In addition, series measurements were performed whereby the association and dissociation properties of formaldehyde or benzoyl-peroxide were described. The results of the experiments proved that the method capable to measure directly these materials and can provide appropriate calibration curves for determination of unknown concentrations.

1. Introduction

Surface plasmon resonance (SPR) is a surface sensitive optical technique that is sensitive to the thickness and refractive index of thin layers at the interface between a metal surface and bulk medium. This instrument method focuses on the determination of biological activity rather than biological structure [1, 2]. SPR is conventionally performed by measuring reflectivity over a series of angles of incident light of fixed wavelength. A minimum in reflectivity occurs at the “SPR angle,” corresponding to the maximal SPR response. The SPR angle varies with the refractive index of the material close to the surface on the side opposite from the reflected light. The FT-SPR is a sensitive, broadly applicable real-time method for analysing thin layers of materials on gold surfaces. SPR reflectivity measurements are surface-sensitive spectroscopic methods that can be used to characterize thickness and refractive index of chemical and any types of films on metal surfaces. FT-SPR measurement is performed at a fixed angel of incident light, and reflectivity is measured over a range of wavelength in the near infrared. In FT-SPR, the minimum in the reflectivity occurs at the „SPR wavenumber.” Since FT-IR spectrometers typically have high wavenumber resolution and precision, and a wide range of reflection angles are available in FT-SPR, FT-SPR is a highly sensitive method with remarkable dynamic range for surface analysis. SPR-based biosensors have been widely developed since the works reported by Liedberg and co-workers during the 1980s [3]. SPR-based immunosensors were described in a recent review by Homola [4]. Their use for the detection of small molecules, in a non-direct format, was the topic of another recent review [5, 6]. The modern sensor technology can improve new possibilities and develop micro and nano surface modified surfaces too [7, 8]. The appearance of different new dental materials could be source of more and more allergic reaction. A part of these materials could behave as allergens. After contact these strange substances could connected to proteins and could work as haptens. The immune system can detect the connected antigens, and it can respond for the presence of these with an abnormal immune response. In similar cases different inflammatory mediators could release eg. histamine, serotonin, leukotriene or prostaglandins.

This is the reason that increasing importance of the more sensitive detection of allergens. The most commonly used polymer in dentistry is the PMMA which is produced from a methyl methacrylate (MMA) monomer during polymerization. The functional groups of residual MMA monomers could become oxidized, and could produce formaldehyde. This small water soluble molecule is one of the most common allergens in the dentistry due to the enhanced reactivity. One another frequent allergen is the benzoyl peroxide. [9, 10] This work examined the possibility of the direct analysis of these allergens. The cardinal starting point was the emergence of the SPR wavelength effect of these materials. This was the reason of the chosen concentration range, what is higher than in a real situation, but appropriate for this model. The investigations of concentration pending of the shifts were the second objective. The time depending of shift of the resonant (SPR) wavenumber could use for illustrate of the association and dissociation properties of these dental allergens.

2. Materials and methods

The formaldehyde (37%) and benzoyl-peroxide were purchase from Sigma-Aldrich Co. LLC. (St. Louis, MO, USA) All materials were used as received, without further purification. The dilution series of formaldehyde were made with bi-distilled water for 0.25%, 0.5%, 1%, 2% and 3.7% concentrations. The solutions of benzoyl-peroxide were created in 0.25%, 0.5%, 1%, 2% and 4% concentrations. All these two dilution series were used for the determination of individual spectra of discrete solutions. In these cases the solutions were flow through the measure chamber, above the thin gold layer while the resonant wavenumber was determined. The serial measurements were perform that the different solutions flow through the chamber for a few minutes one after the other, while in these cases were measured the real-time changes of the resonance wave numbers. The different steps show the different solutions, and these serial measurements could illustrate the association and dissociation properties of these materials

The FT-SPR experiment was performed by using a Nicolet™ 6700 spectrometer with a SPR 100 module. The Nicolet 6700 FT-IR spectrometer was controlled via OMNIC™ software to collect SPR data in reflectance mode. The FT-IR is equipped with a near IR tungsten-halogen light source. The incident angle of light on the prism in the SPR 100 module was then adjusted (to approximately 55°) until the FT-SPR spectral minimum was near 9000 cm-1. A series of SPR spectra were then collected to establish baseline from 11000 – 6000 cm-1 and then each of the spectra were fit with a centre-of-gravity algorithm applied to the bottom 25% of data points, using Thermo's TQ Analyst™ chemometric software package. This curve-fitting routine determined the locations of the minimum for each SPR spectrum. Each curve was average of 16 interferrogramms, the resolution was 8 cm^{-1}, and distances of the data points were 0,964 cm^{-1}. The locations of these FT-SPR minima were then plotted versus time to show the wavenumber shift obtained from analyte binding.

3. Results and discussion

The different concentrations of formaldehyde solutions show different resonant wavenumbers. As the figure 1 a shows from the distilled water to the 3,7% formaldehyde-solutions: 9003 cm^{-1}, 8963 cm^{-1}, 8925 cm^{-1}, 8824 cm^{-1}, 8603 cm^{-1}, 8223 cm^{-1}. The figure 1 b represents the series measurement result, all of levels (horizontal plateau) mean different concentration of formaldehyde and the vertical curves illustrate the association or dissociation characteristic of the material.

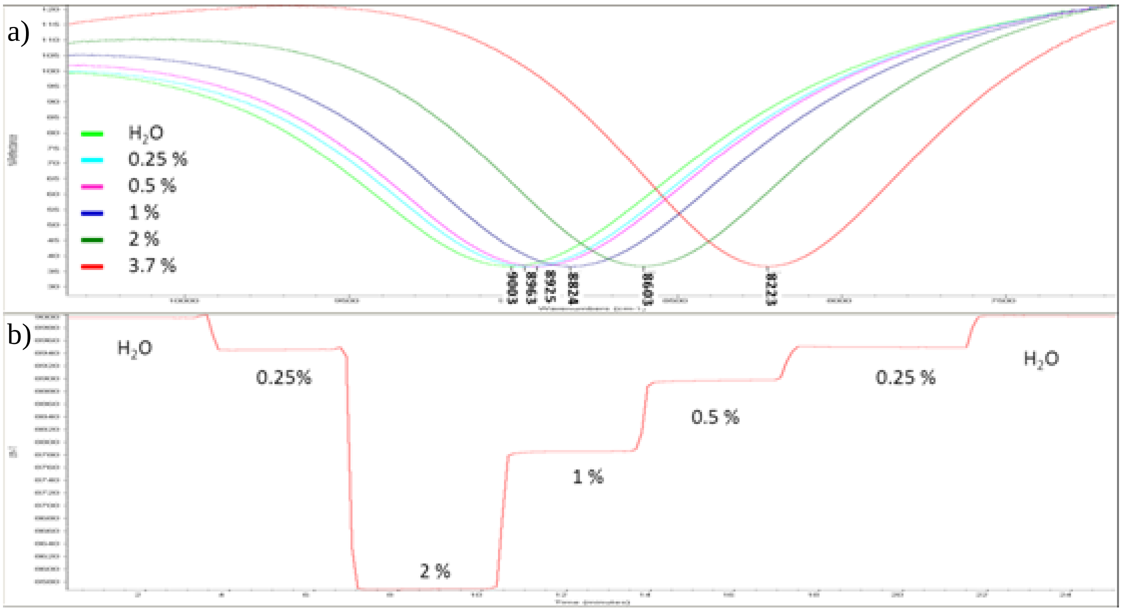

Figure 1. a)) Individual resonant wavenumbers of different concentrations of formaldehyde solutions (legend from top to bottom spectra left to right) b) Resonant wavenumbers shifts of formaldehyde solutions, real-time measurements for illustrate the association and dissociation properties.

The different concentrations of benzoyl-peroxide solutions made using acetone as solvent. The different resonant wavenumbers show on figure 2 a, it shows the FT-SPR spectrum from acetone to the 2% benzoyl-peroxide -solution: as 9041 cm^{-1}, 8924 cm^{-1}, 8822 cm^{-1}, 8587 cm^{-1}, 8085 cm^{-1} and 6742,53 cm^{-1}. The figure 2 b represents the series measurement result, all of levels (horizontal plateau) mean different concentration of benzoyl-peroxide and the vertical curves illustrate the association or dissociation properties.

The bases of analytic determinations are the calibration curves; these can be calculated from the resonant wavenumber shits depending on the different concentrations of solutions. For the calculation of the concentrations of undefined samples these curves must be well determined regard on linearities and standard deviations. The figure 3 a and b show the calibration curves of formaldehyde and benzoyl-peroxide solutions, and represent the equations of trend lines, and the values of R^2.

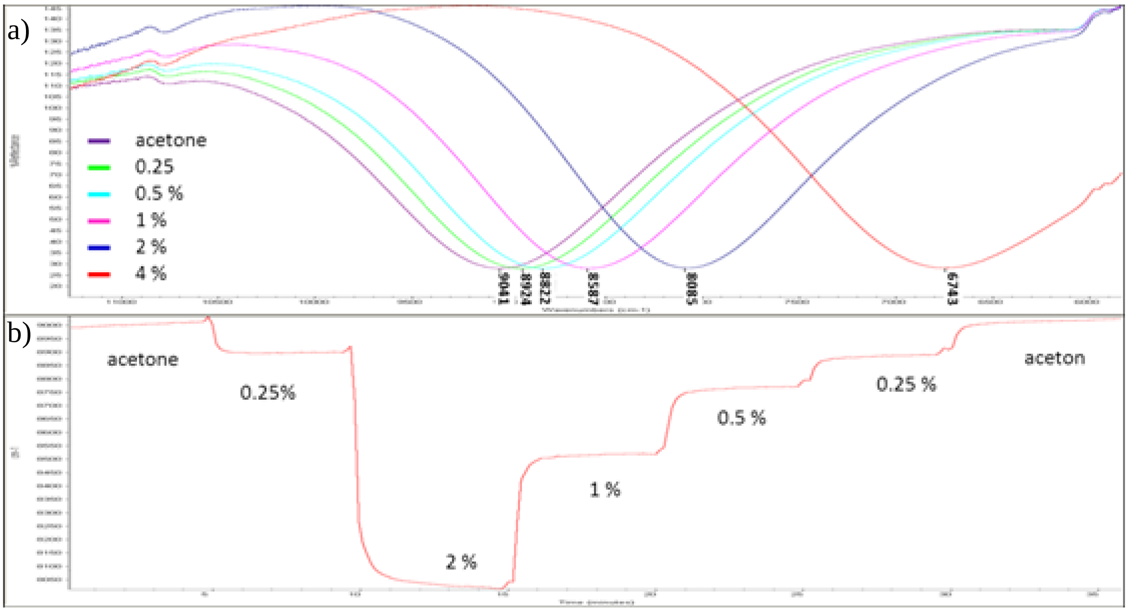

Figure 2. a) Individual resonant wavenumbers of different concentrations of benzoyl-peroxide solutions (legend from top to bottom spectra left to right) b) Resonant wavenumbers shifts of benzoyl-peroxide solutions, real-time measurements for demonstrete the association and dissociation properties

The FT-SPR spectra of formaldehyde show the resonant wavenumbers decreased parallel with the concentrations, and as in the cases of benzoyl-peroxide solutions were observed. The rates of decreasing were more explicit for benzoyl-peroxide solutions in acetone most probably because the changing of refractive index is greater than the formaldehyde solutions in water. The developing of horizontal plateaus of the benzoyl-peroxide solutions shows the differences between the association and dissociation properties of these two materials. All of these phenomena significantly slower than in the cases of the formaldehydes, where the changes from the vertical sections to the horizontal segments are fast and sharp. It could be concluded that the association and dissociation could be played faster and more complete in the cases of formaldehyde solutions. The calculations of the exact values of these constants in this system have not been evaluated. But the illustrated properties showed well the differences of the real time changing of the resonant wavelengths in the cases of these two substances. The changing of SPR wavenumber in the cases formaldehyde solutions were sharp, but the rates were smaller, so the association and the dissociation were faster. In the cases of benzoyl-peroxide solutions the changings were slower, but the rates were larger the emerging of the horizontal part slower and not so explicit.

The calibration curves proved that the determination of unknown amounts of formaldehyde and benzoyl-peroxide is possible in the range of investigation. The linearity is appropriate and the values of R^2 near to 1 enough. The real concentrations, what have to be determined much lower than here, but these experiments showed that this new method is able to measure these materials directly.

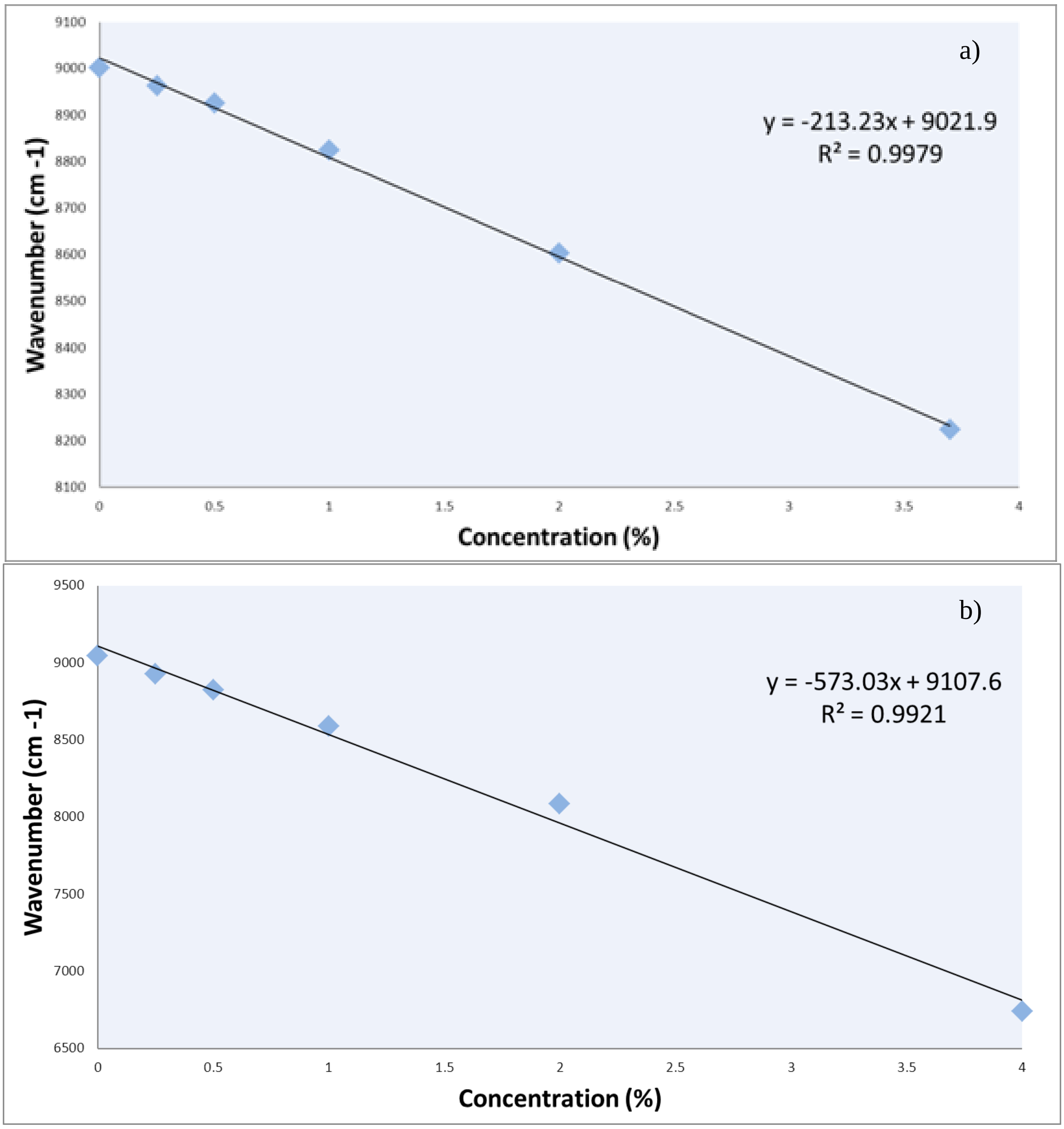

Figure 3. a) Calibration curve calculate based on FT-SPR spectra of formaldehyde solutions. b) calibration curve of benzoyl-peroxide solutions

4. Conclusion

These results show that FT-SPR method can provides a new possibility for the determination of different dental allergens. For further investigation where could be use specific bonding of this substances to the gold surface so the detection limit would be adjustable for the lower region of the concentration, and can avoid the possibilities of matrix effect.

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