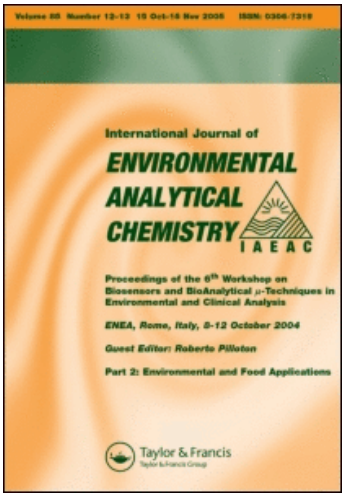

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Resonance Raman Spectroscopy as a Tool for the Detection and Identification of Pollutants in Water

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The use of resonance Raman spectroscopy in water pollution is reviewed. After a short introduction to the technique, the results obtained with this method are illustrated with examples of coloured compounds (such as fabric dyes and food dyes) and non-coloured compounds (such as phenolic compounds and nitrobenzene pesticides). Attention is given to detection limits in distilled and natural water, to identification capabilities and to quantitative determinations. The major advantages are indicated and the problem of interferences due to fluorescence and its reduction are shortly discussed.

KEY WORDS: Water pollution, Raman spectroscopy, dyes, phenols, pesticides.

1. INTRODUCTION

The increase of pollution by hazardous chemicals and man's awareness of their possible dangers have created a great need for suitable techniques for controlling and monitoring air and water pollution. In the last decade, a number of known analytical techniques has been adapted for pollution analysis; Raman spectroscopy is not an exception in this trend. The special characteristics of this technique suggest that it will be a very useful tool for pollution detection, especially in water pollution studies.

Raman spectroscopy is based on light scattering. If monochromatic light (usually in the visible region) is sent through a sample (which contains one or more kinds of molecules in vibrational and rotational states according to the Boltzmann distribution) most of the incident light passes through the sample. A small portion of the light, however, is scattered spherically. This scattering may happen in two different ways:

elastic and inelastic. If the light is scattered elastically, the frequency of the scattered light is the same as the one of the incident light. This phenomenon is called Rayleigh scattering. The light is scattered inelastically when a molecule goes from its original vibrational state to a lower or higher one; the frequency of the scattered light is accordingly higher or lower. This phenomenon is called the Raman effect. The combination of these two phenomena gives rise to a frequency spectrum of the scattered light, dominated by an intense central band at a frequency equal to the one of the incident light, plus a number of weaker bands on both sides of this central band. The lower-frequency lines, called Stokes lines, appear at the same distance from the central band (the Rayleigh line) as the higher-frequency lines, which are called anti-Stokes lines. The intensity of the former are, however, much greater, and usually only this part of the spectrum is measured. For a more detailled description of Raman spectroscopy, the reader is referred to the literature.[1-3]

Raman spectroscopy has a number of advantages in comparison with other techniques used in pollution analysis. By far the major advantage is the fact that the presence of water does not significantly disturb the sensitivity of the effect. Water, even in large quantities, shows only a very weak Raman spectrum. This implies that solutes can be detected in water, even at low concentrations, without previous extractions that are necessary with most other techniques. Furthermore, because of the complexity of the spectrum, it can be used as a fingerprint for identification purposes, an advantage which is lacking in many other techniques.

The application of lasers in Raman spectroscopy during the middle sixties made it possible to obtain Raman spectra at relatively low concentrations. However, the first efforts to apply Raman spectroscopy to pollution studies were not made until the early seventies.

In 1970, Bradley and Frenzel[4] reported a preliminary study on the use of laser Raman spectroscopy for detection and identification of molecular pollutants in water. They reported the detection of benzene in water at concentrations around 50 ppm. In 1972 Baldwin and Brown[5] examined the detection level for some inorganic anions in water. They obtained minimal detectable concentrations between 25 and 75 ppm depending on the type of anion. Recently, using more advanced equipment, Cunningham, Goldberg and Weiner[6] were able to go down to 4–40 ppm for a series of ionic and molecular species in water. A general conclusion that can be drawn from these experiments is that under ideal conditions, the detection limits are hardly low enough to be of practical use. Using the technique in real circumstances, e.g. polluted water, would even be less favourable.

In order to lower the detection level of pollutants in water when using Raman spectroscopy, it is necessary to increase the spectrum intensity without increasing that of water which occurs as a background. Increasing the laser intensity only partially solves the problem. An interesting way of increasing the solute spectrum without increasing that of water is by taking advantage of the resonance Raman effect.

2. RESONANCE RAMAN SPECTROSCOPY AND COLOURED COMPOUNDS

The resonance Raman effect occurs when the frequency of the exciting light beam falls within the absorption band envelope as close as possible to its maximum.[2] In that case, the Raman signal is enhanced by several orders of magnitude (up to 10^6 times) while other compounds, including the solvent, in casu water, do not show this enhancement and exhibit the ordinary Raman spectrum.

This effect has considerable influence on the detection limit of organic pollutants. The detection level is determined by three important factors: the strength of the Raman signal of the compound studied; the intensity of interfering spectra, including the one of water; the strength of the background signal, including the instrumental noise. Since the first one is enhanced by several orders of magnitude when applying the resonance effect and the latter two remain equal, the detection limit will be several orders of magnitude lower and may be expected to be in the low ppb range.

The requirement for the exciting frequency to fall within the absorption band envelope of the compound studied imposes some restrictions on the measurements. Since the exciting light sources (lasers) and the optics of the spectrometer are designed for visible light, the absorption band must have its maximum in the visible region. Therefore, a straightforward application can only be done on coloured compounds.

The first investigations on the applications of resonance Raman spectroscopy were carried out in 1978 by Van Haverbeke *et al.*[7] This study led to detection limits of 30–50 ppb for industrial fabric dyes, which is approximately three orders of magnitude lower than those of conventional Raman spectroscopy. Comparison with UV-visible spectrophotometry shows the same sensitivity for both techniques. Moreover, the authors were able to obtain spectra suitable for identification purposes at concentrations between 75 and 175 ppb. Spectra of the four dyes examined at concentrations close to the latter value are shown in Figure 1. They als also tested the method under actual conditions using artificially "polluted" river water. A spectrum at a

concentration of 300 ppb clearly showed the presence and revealed the identity of the dye as is shown in Figure 2. A similar study on pesticides gave analogous results.[8]

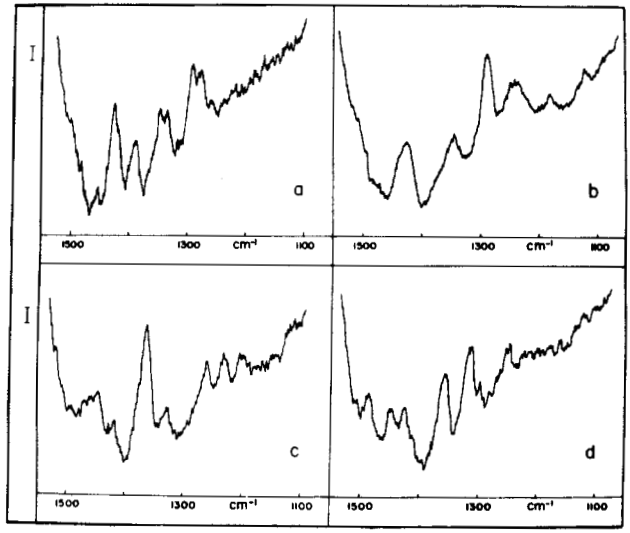

FIGURE 1 Resonance Raman spectra of four fabric dyes in water. (a) Superlitefast Rubine (88 ppb); (b) Procion Red (192 ppb); (c) Lyrazol Fast Red (210 ppb); (d) Direct Red 83 (190 ppb).[16]

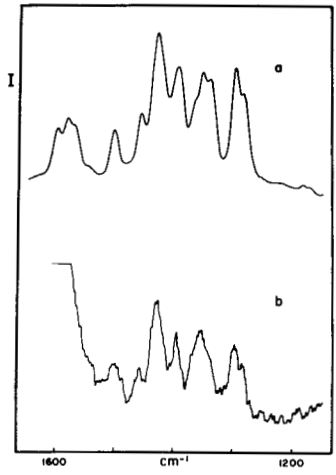

FIGURE 2 Resonance Raman spectra of Superlitefast Rubine (a) in distilled water (24.3 ppm), (b) in river water (288 ppb).[16]

Quantitative measurements can also be done with this technique, as has been demonstrated for the same compounds. However, some very important facts should be considered here. Although it is theoretically possible, it is very difficult to perform absolute measurements of Raman band heights or intensities. The main reason for this is the uncertainty regarding the efficiency of the spectrum analyzer (monochromator) and the detection system, and also the reproducibility of the optical sample arrangement. Therefore, it has become common use to measure the relative height or intensity of a band of the compound studied versus one of an internal standard.

The next problem therefore is the choice of the internal standard. Since we always have the same solvent (water) present in more or less the same amount, we can easily use one of the two bands of water (around 1600 and 3500 cm^{-1}) as internal reference band. The disadvantage of this choice is the fact that both bands are extremely broad, which tends to introduce errors in their height and area calculations.

For both sample and reference bands it is preferable to use integrated band intensities instead of the band heights, since the height is much more sensible to differences in monochromator slit variations than the integrated intensity. Integrated intensity calculations can be done by several methods with varying accuracy.[9] We have been most successful with those based on band contour analysis using asymmetrical mixed Gauss-Lorentz profiles carried out with a computer.[10]

When one is using resonance Raman spectroscopy, the incident as well as the scattered light falls within the absorption band envelope. This indicates that we have to account for the absorption of light by the sample. The amount of light reaching the point of scattering is the same for both sample and reference (H_2O) molecules. However, since the frequencies of the Raman bands of sample and references are different, the effect of absorption will be different on each; their intensity ratio is expressed by the following equation:

$$\frac{I_{\text{sampl}}}{I_{\text{ref}}} = (\text{Const})\, c_{\text{sample}} \exp(-(\varepsilon_s - \varepsilon_r)\, l c_{\text{sample}})$$

wherein ε_s and ε_r are the molar absorptivities of the sample at the frequencies of the sample and reference band, respectively, and l is the optical path length between the scattering point and the end of the sample cell. As can be seen, an exponential deviation from a straight line is obtained.[11] This relationship can still be used for quantitative measurements by constructing a calibration curve. However, care must be taken to do all measurements in the same optical arrangement, so that l

remains constant. This requires rigid sample holders and perfectly matched cells, or the use of one single cell.

An approach to continuous monitoring of natural water by means of Raman spectroscopy has been proposed by Van Haverbeke and Brown.[12] They mounted a flow cell in the standard illumination chamber of the spectrometer. By means of a continuous pumping system and tubing, water is drawn from the source to be monitored and passed through the cell. Comparison with classical Raman measurements showed that the background is enhanced and the signal to noise ratio lowered by approximately 30%. This is caused by the flow of the solution through the cell. Experiments have shown that a cell with square cross-section gives the best results. The sensitivity is consequently 30% less than for conventional measurements.

A practical example of the use of resonance Raman spectroscopy is the determination of food dyes in food, e.g. candy. Here the emphasis is not so much on low detection limits, since at least 1 ppm is necessary to produce any visible colour (which is the primary objective). Much more attention is given to the quantisation and identification capabilities.

When the resonance Raman spectra of the red, orange and yellow food dyes, listed by the European Economic Comminity are recorded, some important conclusions may be drawn. First of all, it appears that the natural food dyes (e.g. cochineal, lactoflavin, etc.) do not show a noticeable Raman spectrum even at relatively high concentrations, and therefore cannot be measured by this method. Furthermore, every artificial food dye shows a spectrum that is very different from that of the others. From this it follows that artificial dyes can be detected in the presence of natural dyes without interference and that they can be identified unambiguously. In Figure 3 the spectra of the aqueous solution of a commercial yellow bubble gum (three balls from which the outer, coloured layer is dissolved in 100 ml of water) and of a 10 ppm solution of tartrazine (E102) are given. Both spectra agree very well. Quantitative determination revealed an amount of approx. 10 mg tartrazine per bubble gum ball.

Comparison with UV-Vis spectroscopy indicates a similar sensitivity, but the identification of the dye is far more accurate with the resonance Raman technique.

3. NON-COLOURED POLLUTANTS

So far, the method proved only to be useful when coloured substances have to be measured. To extend the method to compounds that do no not show any visible absorption, one can go two ways. Either one uses UV

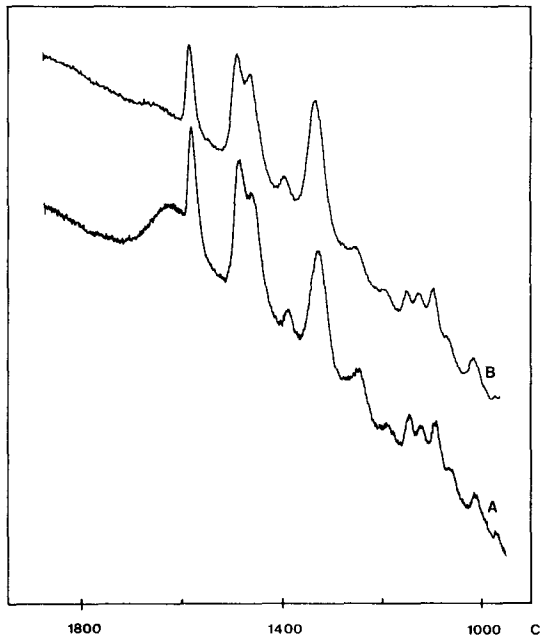

FIGURE 3 Resonance Raman spectra of (a) tartrazine in water (10 ppm); (b) aqueous solution of yellow bubble gum (see text).

lasers and spectrometer optics, so that all UV-absorbing compounds can be measured, or one transforms the non-coloured compounds into coloured ones by means of derivatisation methods. We prefered the latter technique, because it requires no extra investment in spectrometer equipment (UV laser and optics) and is more selective, although it involves some extra sample preparation time.

This methos has first been investigated for phenolic pollutants.[13] Before doing the actual recording of the Raman spectra, one has to examine the available derivatisation methods. The requirements that have to be met to obtain derivatives suitable for resonance Raman spectroscopy are:

i) The method must give derivatives that exhibit strong resonance Raman spectra. This implies that the absorption maximum must be close to the laser line used and have an absorptivity as high as possible.

ii) The dye that is formed must be stable in the intense laser beam.

iii) The dye must exhibit as little fluorescence as possible as this interferes with the Raman spectrum.

Using these requirements, we found the best results for coupling the phenolic compounds with the diazonium salt of 4-nitroaniline in alkaline

medium. The absorption maximum (477 nm) is pretty close to the 488 nm Ar^+ laser line. The resonance Raman spectrum is relatively strong and the fluorescence in the used spectral region is moderately low. Furthermore, the dye is pretty stable in the laser beam.

In Figure 4 the spectra of 1 ppm solutions of phenol, *o*- and *m*-cresol

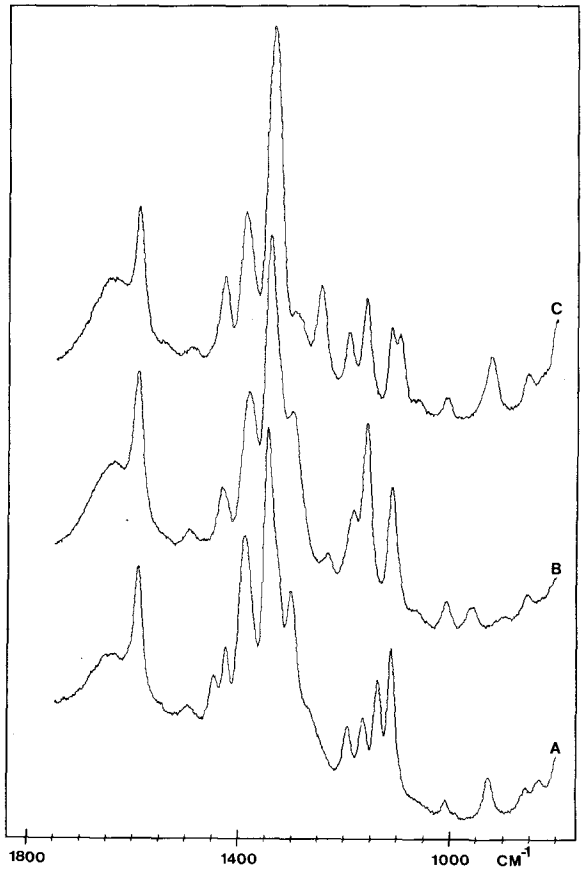

FIGURE 4 Resonance Raman spectra of phenolic compounds in water. (a) phenol (1 ppm); (b) *o*-cresol (1 ppm); (c) *m*-cresol (1 ppm).[17]

are displayed. As can be seen, the spectra are relatively clear and smooth. For these compounds and many others that have been investigated, detection limits between 10 and 20 ppb were found. The figure also illustrates the changes in the spectrum when a methyl group is introduced in the molecule or when it is shifted from one position to another. This

indicates that the resonance Raman spectra can very well be used for identification purposes.

A similar study was performed for pesticides based on the nitrobenzene structure.[14] In this case, the best derivatisation method proved to be the reduction of the nitro group, followed by diazotation and coupling with *N*-(1-naphthyl)-ethlenediamine. Again, detection limits below 20 ppb were found and the spectra showed enough detail to allow differentiation of the different pesticides. In both studies, quantitative studies were carried out by means of spectrum analysis and a calibration curve. Concentration determinations could be done within 5% accuracy.

When applying this technique to natural water samples that were doped with the compound studied, we observed an increase of the detection limit to 50–100 ppb, depending on the sample source. This is due to the appearance of fluorescence exhibited by other organic compounds already present in the water sample.

4. FLUORESCENCE AND HOW TO DEAL WITH IT

The most serious problem in recording resonance Raman spectra is the occurrence of fluorescence. Fluorescence may originate from different sources in environmental samples. The compound itself may exhibit fluorescence. If this is a colured pollutant, it may be hard to perform good measurements. If the compound is a derivative of a non-coloured pollutant, preference should be given to another derivatisation procedure. Further, the presence of other organic compounds in the natural water sample may be the cause of this fluorescence.

Several methods have been proposed to reduce the influence of the fluoresence from the water sample on the spectra.[1] They include instrumental as well as chemical methods. The most important among these are derivative spectroscopy and time-resolved Raman spectroscopy. In the course of our investigations, we have obtained excellent results by treating natural water samples containing phenolic compounds with Al_2O_3 in acidic medium after the derivatisation procedure.[15] The results of this procedure are given in Figure 5.

5. CONCLUSION

From the foregoing, it may be concluded that resonance Raman spectroscopy is a promising technique in water pollution measurements. Detection limits in the mid-ppb range can be obtained for both coloured

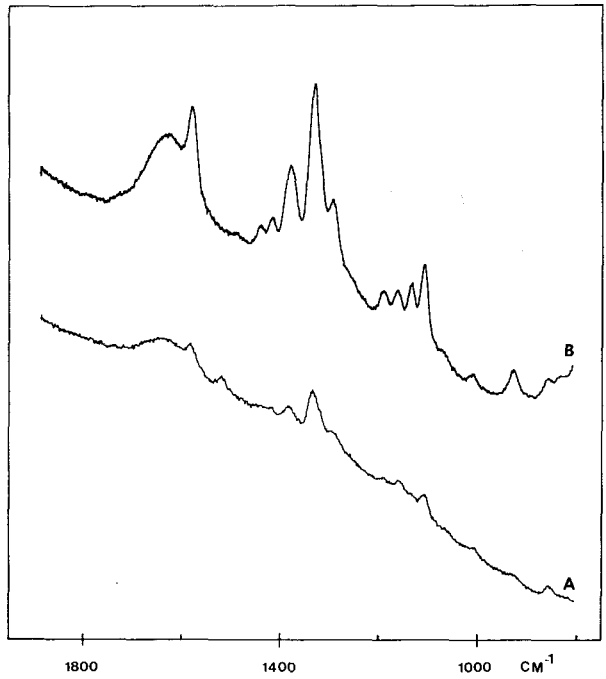

FIGURE 5 Resonance Raman spectra of 1 ppm phenol in rural pond water: (a) untreated; (b) after Al_2O_3 treatment (see text).

and derivatised non-coloured pollutants. Quantitative measurements can be performed easily and the method is suitable for monitoring purposes. The fluoresence problem can be avoided by using appropriate instrumentation or be simple chemical procedures.

The present detection limits are, however, still too high for use in environmental analysis. Many organic pollutants can be harmful in concentrations around 1 ppb, especially those that can be concentrated in the food chain by factors of thousand or more. In this view, further investigations are planned using new instrumental designs that may further lower the detection limit towards the low- and sub-ppb range. The range of detectable compounds is currently being extended and the handling of mixtures of similar compunds is investigated by using computer-aided spectrum analysis and column chromatography.

References

1. S. K. Freeman, *Application of Laser Raman Spectroscopy* (J. Wiley & Sons, New York, 1974).
2. H. J. Bernstein, *Advan. Raman Spectr.* 305 (1972).
3. T. R. Gilson and P. H. Hendra, *Laser Raman Spectroscopy* (Wiley Interscience, New York, 1970).
4. E. B. Bradley and C. A. Frenzel, *Water Res.* **4,** 125 (1970).
5. S. F. Baldwin and C. W. Brown, *Water Res.* **6,** 1601 (1972).
6. K. M. Cunningham, M. C. Goldberg and E. R. Weiner, *Anal. Chem.* **49,** 70 (1977).
7. L. Van Haverbeke, P. F. Lynch and C. W. Brown, *Anal. Chem.* **50,** 315 (1978).
8. R. J. Thibeau, L. Van Haverbeke and C. W. Brown, *Appl. Spectr.* **32,** 98 (1978).
9. L. Van Haverbeke and H. O. Desseyn, *Ind. Chim. Belge* **39,** 142 (1974).
10. L. Van Haverbeke, C. W. Brown and M. A. Herman, *Appl. Spectr.* **32,** 90 (1978).
11. L. Van Haverbeke, D. Goldfarb and C. W. Brown, *Appl. Spectr.* Submitted for publication.
12. L. Van Haverbeke and C. W. Brown, *American Lab.* **10,** 62 (1978).
13. L. Van Haverbeke and M. A. Herman, *Anal. Chem.* **51,** 932 (1979).
14. L. Van Haverbeke, J. F. Janssens and M. A. Herman, In preparation.
15. L. Van Haverbeke, J. F. Janssens and M. A. Herman, *J. Raman Spectr.* Submitted for publication.
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