POLISH JOURNAL OF FOOD AND NUTRITION SCIENCES
Pol. J. Food Nutr. Sci. 2003, Vol. 12/53, SI 2, pp. 100-107

DIFFUSE REFLECTANCE SPECTROSCOPY IN PHOTOCHEMISTRY OF OPAQUE FOOD PRODUCTS – METHODS AND APPLICATIONS

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Key words: diffuse reflectance, laser flash photolysis, photochemistry, non–transparent samples

The applicability of diffuse reflectance spectroscopic techniques to the studies of photochemical degradation of foodstuffs is discussed. Experimental methods and the theoretical base for their quantitative usage are explored. Some examples of practical application of the techniques for photochemical studies in heterogeneous opaque systems are presented. The methods discussed provide essential parameters of the foodstuffs, that cannot be assessed otherwise.

INTRODUCTION

Gaining a better understanding of photochemical processes occurring in food is presently of great interest to researchers, consumers and manufacturers. There exist numerous processes which cause degradation of food quality under light exposure. Among the methods applied for the study of such light-induced phenomena, those used in photochemistry are of primary interest. However, most food products are opaque or strongly light scattering, thus the traditional photochemical techniques often fail. Classic laser flash photolysis, for instance, is primarily used in transparent media; however, it is inapplicable to opaque systems. The significance of flash photolysis as a way of studying and observing transient species in transparent media, has been recognized by the Nobel Prizes awarded in 1967 to Lord George Porter, Ronald G.W. Norrish and Manfred Eigen, and in 1999 to Ahmed Zewail. Diffuse reflectance laser flash photolysis (DRLFP) extends the advantages of laser flash photolysis to non–transmissive media enabling transient spectra and kinetics of photoinduced elementary reactions to be recorded in opaque and/or strongly scattering environments. Since its invention twenty years ago by F. Wilkinson at Loughborough University, UK [Wilkinson, 1981; Wilkinson & Kelly, 1989], diffuse reflectance laser flash photolysis has remained one of the most important tools to study photoinduced processes in opaque media. There is also a growing realization that most technological applications of photochemistry involve opaque systems, and hundreds of applications have appeared — to name just a few, in medicine, biology, pharmaceutical analysis, food analysis, forensic science, photography, environmental research, paper, photosensitized polymerization, *etc*. The study of photochemical action on foodstuffs has a long history; the “lightstruck” flavour of beer as a result of solar irradiation was first noted by Lintner in 1875 [Lintner, 1875]; similar effects were noted in other beverages such as wine and milk [Spikes, 1981]. Other studies have focussed on the environmental fates of herbicides and pesticides [Parlar, 1990, 1991] and other materials used in food production, and of course the process of photosynthesis has been studied comprehensively [Hall & Rau, 1999]. Photoinduced oxidation processes have been studied extensively for many years [Wilkinson *et al*., 1993b, 1995; Redmond & Gamlin, 1999]; such photooxidation phenomena are linked to photoinduced rancidity of foodstuffs, mainly *via* oxidation of unsaturated fats [*e.g*. Frankel, 1998]. In our presentation, a DRLFP system is described, including instrumentation and experimental methods applicable to opaque systems, and the basis of the diffuse reflectance techniques. Over the years, other steady–state and time–resolved spectroscopic techniques have been modified to address non–transparent samples. Prospects and benefits of photochemical studies are discussed, along with case studies covering different possible applications. Results on complex systems of practical importance are presented, including the spectroscopy and photochemistry of flavins in solid matrices, and some metal complexes of alkaloids in their solid state. The examples presented show a wide range of potential applications of optical spectroscopic techniques in turbid and opaque media to studies of photochemical degradation phenomena of food products.

EXPERIMENTAL TECHNIQUES AND BACKGROUND

In reflectance spectroscopy, the Kubelka–Munk remission function $F(R)$ [Kubelka & Munk, 1931] replaces the Lambert-Beer law (Figure 1). In the Kubelka–Munk formulation the remission function for an ideal diffuse scatterer, which is optically thick at the wavelength of choice, and with an homogeneous distribution of absorbers throughout the sample, is given by the Kubelka–Munk function:

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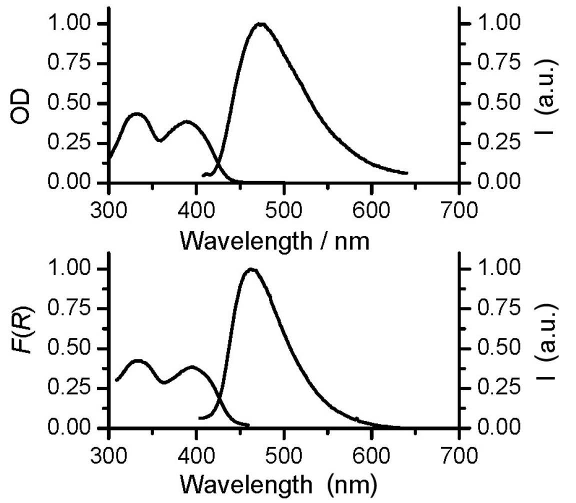

FIGURE 1. Spectra of 7-methylalloxazine ground state absorption in acetonitrile solution (top panel) and ground state diffuse reflectance spectrum on cellulose at a loading of 1.0 mg g^{-1} (bottom panel). Corresponding normalized fluorescence emission spectra are also shown.

$$F(R) = \frac{(1-R)^2}{2R} = \frac{K}{S} \qquad (1)$$

where R represents the observed diffuse reflectance from the surface of the sample, K and S are absorption and scattering coefficients, respectively. It should be noted that the values of $F(R)$ are proportional to K, which is proportional to the absorber concentration. Some other functions for qualitative treatment of the ground state, such as R, log R, $1/R$, and –log R, have been proposed. These functions may be used instead of $F(R)$ because their maxima correspond to those in the Kubelka–Munk function. However, for quantitative simulation of an absorption spectrum of a sample in a scattering environment, the use of Kubelka–Munk function is essential.

Luminescence spectroscopy of highly scattering samples studied both in the pulsed excitation mode and in steady–state excitation is virtually identical to that in liquids, although restricted to front-surface geometry. However, much more attention has to be paid in scattering samples to reabsorption and reemission phenomena, aggregation of the adsorbates, slow reorganization dynamics in the adsorbate/adsorbent environment, cage effects, energy transfer *etc.* [Oelkrug, 1994; James *et al.*, 1985; Liu & Ware, 1993; Liu *et al.*, 1993a, b].

Amongst time-resolved techniques, traditional laser flash photolysis has been increasingly applied to different transparent media; however, it fails in opaque systems. Diffuse reflectance laser flash photolysis extends the advantages of laser flash photolysis to non–transmissive media and enables transient spectra and kinetics of photoinduced elementary reactions to be determined. The diffuse reflectance laser flash photolysis equipment is similar in principle to that used in conventional flash photolysis experiments, but the geometrical arrangement of the laser beam, the analysing light and sample is different. The schemes in Figure 2 show two possible systems, for transparent and opaque samples, appropriate for laser flash photolysis with nanosecond time resolution. Diffuse reflectance laser flash photolysis has become the dominant tool to detect short–lived intermediates and thus, to elucidate elementary reaction steps, on timescales ranging from femtoseconds [Asahi *et al.*, 1998] to hours and days.

In both modes of flash photolysis experiments, it is important that the analysing light probes only the spot excited by the laser beam. In the case of opaque materials, it is extremely important that no mirror (or specular) reflection of the excitation beam reaches the slit of the analysing monochromator. The information about transients is taken from the diffuse reflectance signal of the analysing light. Figure 3 presents typical examples of data recorded using diffuse reflectance laser flash photolysis.

Kinetic analysis, and of course time–resolved spectroscopic analysis, require a quantitative treatment of the concentration change of the transients. Wilkinson and others [Kessler *et al.*, 1983; Oelkrug *et al.*, 1987; Wilkinson & Kelly, 1989] have introduced the function of time $\Delta J_t/J_0 = 1\text{-}R_t$, where J_0 is the initial reflectance prior to

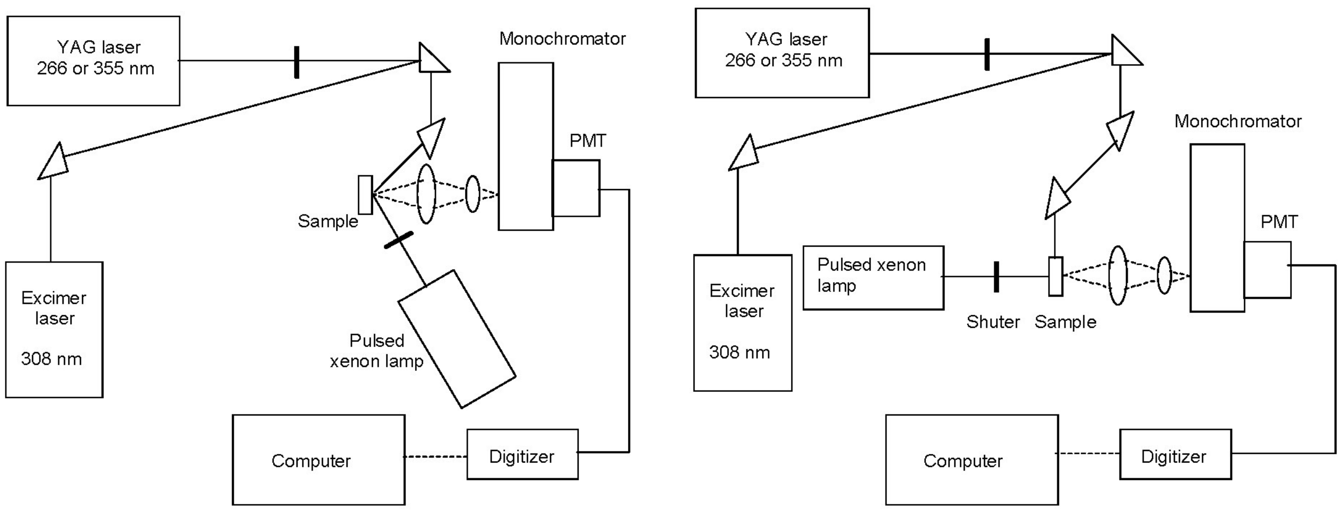

FIGURE 2. Experimental setup for diffuse reflectance laser flash photolysis measurements (left), experimental setup for conventional flash photolysis experiments (right).

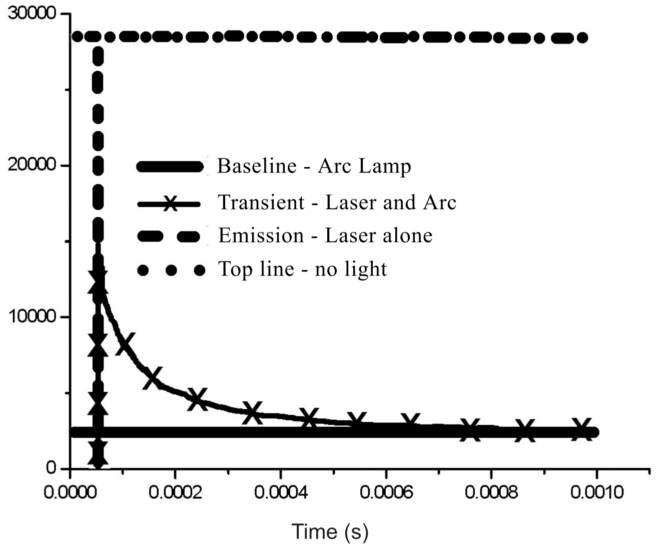

FIGURE 3. A typical set of traces obtained using the diffuse reflectance laser flash photolysis equipment.

laser excitation, and ΔJ_t is the difference between J_0 and J_t, which is the reflectance of the sample at time (t) after the excitation pulse. R_t is the relative reflectance defined by the ratio of the reflectance of the sample at the analysing wavelength to the background reflectance. Transient concentration was shown to be directly proportional to $\Delta J_t/J_0$, for the initial transient absorption values below 0.05. However, the detected $\Delta J_t/J_0$ variation depends not only on the decay kinetics of the absorbing transient but also on the concentration profile of the transient species below the irradiated surface. The above function is only applicable when the transient concentration decreases exponentially with the penetration depth into the opaque sample. Such an exponential decrease is more likely for low-intensity excitation, high initial concentrations of ground-state molecules and low absorption coefficients at the excitation wavelength. In the studies presented, the ratio $\Delta J_t/J_0$ never exceeded the 0.05 limit and, thus the $\Delta J_t/J_0$ function was used to analyse both the transient spectra and the decay kinetics.

Particular effort has been made to describe the relaxation kinetics of electronic excited states of polyatomic molecules adsorbed onto solids [*e.g.* Barra *et al.*, 1991; Sikorski *et al.*, 1997; Kamat *et al.*, 1993; Lei *et al.*, 1992, Ramamurthy & Eaton, 1994; Barra & Scaiano, 1995]. In contrast to homogenous solutions, the heterogeneous nature of the adsorption sites in opaque materials is often a reason for complex kinetics. Among existing approaches, the Albery model has been particularly successful [Albery *et al.*, 1985]. In a heterogeneous system, the model considers an observed decay profile as a sum of contributions from different subsets of a microscopic species, each subset existing in a slightly different environment. The model assumes that the free energy of activation, $\Delta G^* = \Delta G^* - \gamma x RT$, is distributed normally around the mean value ΔG^*. The parameter γ is the relative distribution width. When γ=0, there is no dispersion and the kinetics will behave in a classical homogeneous fashion. The assumed distribution of the free energy of activation leads to a log-normal distribution of the decay rate constants. This distribution can be characterized by an average rate constant, k. The dispersion in the first-order rate constant for $-\infty \leq x \leq \infty$ then becomes:

$$\ln(k) = \ln(k) + \gamma x \qquad (2)$$

Making the integration over the normal distribution, $\exp(-x^2)$, and additionally assuming that the luminescence intensity is proportional to the probe's excited-state concentration, we obtain the kinetic equation in the following form, after Albery and Thomas:

$$\frac{I_t}{I_0} = \frac{\int_{-\infty}^{+\infty} \exp(-x^2)\exp[-\overline{kt}\exp(\gamma x)]dx}{\int_{-\infty}^{+\infty} \exp(-x^2)dx} \qquad (3)$$

where

$$\int_{-\infty}^{+\infty} \exp(-x^2)dx = \Pi^{1/2}$$

Here I_t and I_0 are the luminescence intensity after the excitation pulse at times t and t = 0, respectively. An analysis of the decay data using this model provides information about the mean, k, and the width, γ, of the log-normal distribution of the rate constants. At γ=0, the model reproduces the *classical* well–defined single–exponential decay.

Exponential series lifetime distribution analysis is also frequently used [Siemiarczuk & Ware, 1987, 1989; Siemiarczuk *et al.*, 1993; Liu *et al.*, 1993a; Liu & Ware, 1993]. This analysis has an inherent advantage of not requiring *a priori* any specific kinetic model with a given set of adjustable parameters. The only limitation of this approach is that the respective processes should be monomolecular or pseudo–monomolecular with the quencher concentration significantly exceeding that of the quenched molecules, which is usually the case. The exponential series lifetime distribution analysis has been performed using the nonlinear least–squares fitting algorithms, the more complicated software making it less popular.

The equipment required for the measurements (Figure 2) is fundamentally the same as used in transmission pulsed photolysis studies, and usually relies on a pulsed laser as a source of photolysing light, which often determines the system time resolution. Another crucial component is a high-intensity probe light source. This source must have higher intensities in diffuse-reflectance as opposed to transmission studies, due to problems associated with the excitation laser pulse scattering and the sample emission. Its is preferable to use double monochromators with low stray light in a diffuse reflectance setup, in order to further reduce interference from scattered laser light and sample emission. The necessary components may be acquired from various vendors operating on the market of scientific and laser equipment and then integrated. Alternatively, several vendors like *Applied Photophysics* or *PRA* provide integrated systems with the necessary control and data processing software included.

SELECTED APPLICATIONS

Flavins and their derivatives

The term ‘Flavins’ refers to the 10-substituted 7,8-dimethyl-2,3,4,10-tetrahydrobenzo[*g*]pteridine-2,4-diones, among which are the natural coenzymes: riboflavin, FMN and FAD. Lumiflavin, Lfl, (7,8,10-trimethylbenzo[*g*]pteridine-2,4(3*H*,10*H*)-dione), is another representative of flavins. Isoalloxazines (isoalloxazine: 10-substituted 2,3,4,10-tetrahydrobenzo[*g*]pteridine-2,4-dione) and especially flavins, possess the yellow chromophore characteristic of flavoproteins – enzymes occurring widely in animals and plants. Alloxazine, All, (benzo[*g*]pteridine-2,4(1*H*,3*H*)-dione) and lumichrome, Lch, (7,8-dimethylalloxazine=7,8-dimethylbenzo[*g*]pteridine-2,4(1*H*,3*H*)-dione) are representative of alloxazines, a class of nitrogen heterocycles related to lumazine and flavins. Iso- and alloxazines are closely related compounds, representing two classes of nitrogen heterocycles with active centres at N(10), N(5), N(3) and N(1), and at both carbonyl oxygens at C(2) and C(4), yet the spectroscopic and photophysical properties of these two groups are quite different. The structure of some biochemically functional forms of flavins is presented in Figure 4. Alloxazines are well known as photochemical decomposition products of flavins. Substituted alloxazines, mainly lumichromes, have been found in many biological materials. For example lumichrome, as a product of photodecomposition of riboflavin, has been found in milk and could contribute to its photodecomposition [Toyosaki & Hayashi, 1993]. In a recent report on the dynamics of photon–induced degradation and fluorescence of riboflavin microparticles riboflavin was found to convert easily into lumichrome [Pan *et al.*, 2001].

We have used diffuse reflectance spectroscopy to study flavins and alloxazines supported on different solids including cellulose [Sikorski *et al.*, 2002a, b, 2003; Sikorski, 2002b], cyclodextrins [Mir *et al.*, 1997] and some others [Sikorski *et al.*, 1999a, 2002a].

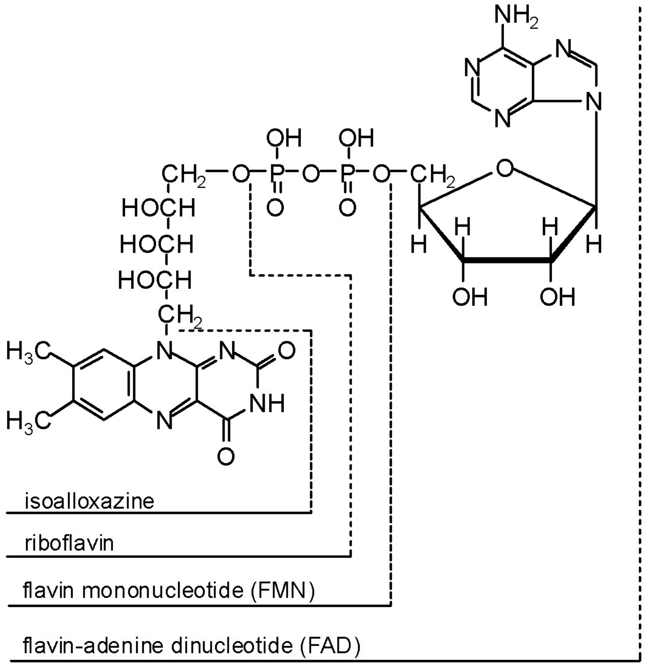

FIGURE 4. Structure of biochemically functional forms of flavins: isoalloxazine, riboflavin, flavin mononucleotide (FMN) and flavin-adenine dinucleotide (FAD).

An example of steady state and time resolved studies of 6-methylalloxazine adsorbed onto microcrystalline cellulose is shown in Figure 5. As common for inhomogeneous systems, we applied exponential series lifetime distribution analysis to the fluorescence decay kinetics without any preliminary assumptions as to the number of the distribution modes. Fluorescence decays were analysed with a PTI Time-Master Pro analysis package using the lifetime distribution algorithm based on the exponential series method [Siemiarczuk *et al.*, 1990]. The package uses a sum of up to 200 exponential functions with fixed logarithmically spaced lifetimes, with the preexponential factors recovered by the least–squares minimisation procedure. Representative results showing the lifetime distribution of 6-methylalloxazine is presented in Figure 5. This lifetime distribution has three maxima at about 0.55 ns, 1.2 ns and 4.8 ns. Fluorescence decay data allowed identifying three types of interaction between 6-methylalloxazine and microcrystalline cellulose.

Additional information about flavins and alloxazines on cellulose was provided by the time–resolved diffuse reflectance laser flash photolysis method which enables detection of short–lived transient species produced by photon absorption in solid materials. The diffuse reflectance laser flash photolysis was able to detect two transient species. The short–lived species has a lifetime of the order of microseconds and responds to oxygen, suggesting that this is the lowest alloxazine triplet. Typical transient absorption spectra generated by 6-methylalloxazine and 3-methyllumiflavie are shown in Figure 6.

Solid metal complexes of sparteine

Sparteine, a naturally occurring member of the lupine alkaloid family, is a representative of one class of proton sponges. Different types of studies have covered various aspects of sparteine and its derivatives, we may recall analytical usage in determination

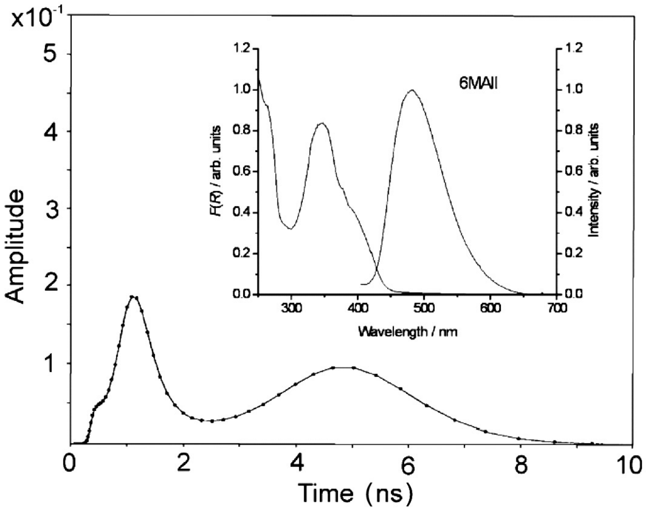

FIGURE 5. Fluorescence lifetime distribution for 6-methylalloxazine and the corresponding ground–state diffuse reflectance absorption and fluorescence spectra.

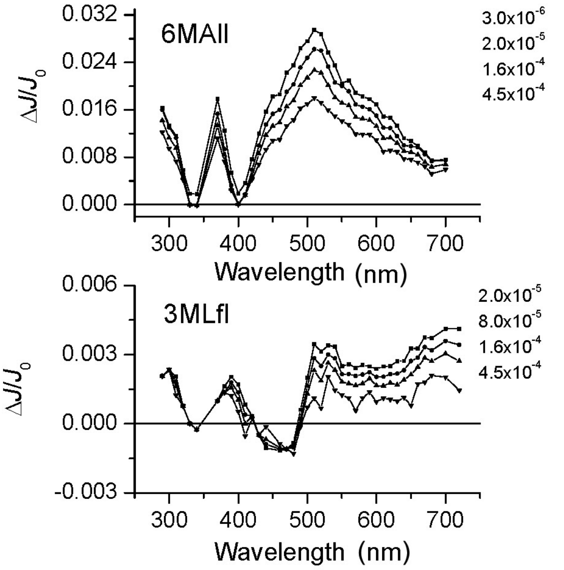

FIGURE 6. Time–resolved diffuse reflectance laser flash photolysis spectra of 6-methylalloxazine, 6MAll, 7-methylalloxazine, 7MAll, and 3-methyllumiflavin, 3MLfl, at 0.3 mg/g loading on cellulose at room temperatures in deaerated samples. Excitation is at 355 nm. Delay times are indicated on the panels.

of cations and identification of amines, through its role in living organisms, and finish with the applications in asymmetric synthesis [Pippel *et al.*, 1998; Remenar *et al.*, 1997a, b]. Sparteine is a naturally occurring chiral diamine which, depending on its conformational and configurational arrangement, is responsible for the bitter taste. The structure of sparteine, with two nitrogen atoms specifically placed in space, makes it an excellent ligand for metal complexes [Toda *et al.*, 1983], see Figure 7 [Wiberg & Bailey, 2000; Kuroda & Mason, 1977; Lopez *et al.*, 1998].

Diffuse reflectance offers a simple method to extend the measurement capabilities of the UV-Vis-NIR spectroscopy to solid opaque samples, requiring minimal or no sample preparation. In our studies, we synthesised complexes between (–)-sparteine, its derivatives (2-methyl- and 2-oxosparteine and 2-cyano-2-methylsparteine) and metal salts: copper, cobalt and nickel chlorides, $CuCl_2$, $CoCl_2$, and $NiCl_2$, and lithium perchlorate, ($LiClO_4$). The complexes were characterised by UV-Vis-NIR diffuse reflectance, IR, NMR and mass spectroscopy, and also by elemental analysis [Jasiewicz *et al.*, 2002, 2003a, b]. Almost all the complexes studied present the 1:1 stoichiometry, the 2-cyano-2-methylsparteine complex with $LiClO_4$ being an exception with 1:2 stoichiometry.

Diffuse reflectance absorption spectra of solid complexes, and of sparteine derivatives themselves, were recorded on KBr. Diffuse reflectance absorption spectra of sparteine and its derivatives exhibit a single absorption band with the maximum at about 218 nm. Complexation with the metal salts studied caused significant changes in the diffuse reflectance spectra, as compared to the spectra of the corresponding sparteins. The changes can be easily seen in Figure 8. The most intriguing and obvious changes occurred in the NIR region, where two new broad bands appeared. Our findings demonstrated a distinct effect of complexation on spectra of sparteine and its derivatives with metal salts, recorded on solid supports [Jasiewicz *et al.*, 2003a, b].

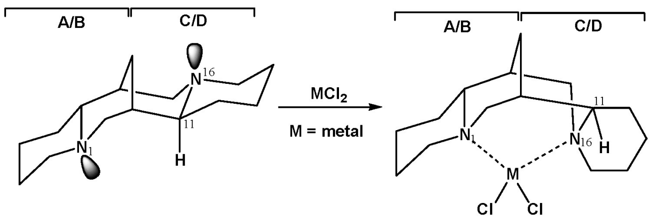

FIGURE 7. (–)-Sparteine and its conformation-configuration arrangements.

Co(II) in tetrahedral symmetry is expected to have three spin–allowed *d-d* transitions in the Vis-NIR region, and these are from the ground state $^4A_2$ to the $^4T_1(P)$, $^4T_1(F)$, $^4T_2(F)$, and states [Ferreira da Silva, 1999]. The strong spin-orbital coupling in the tetrahedrally coordinated Co(II) complexes results in the splitting of each of the orbital crystal field terms into three spin-orbital levels [Ferreira da Silva, 1999]. The complex studied should have a distorted tetrahedral coordination sphere [Lee *et al.*, 1998a, b; Kuroda & Mason, 1977] and thus a spectrum close to that of a tetrahedral system. For comparison, a spectrum of tetrahedral cobalt(II) contains visible bands at 625-500 nm ($^4A_2(F) \rightarrow {}^4T_1(P)$) transition, and NIR bands at 3300-2500 nm and 1700-1400 nm, the respective $^4T_2(F)$ and $^4T_1(F)$ transitions [Ferreira da Silva, 1999].

Other studies

Some other areas where we used diffuse reflectance include spectroscopy and photophysics of selected organic dyes on opaque solid supports, such as photochemistry of thioketones on solid matrices [Sikorski *et al.*, 1997, 1999b; Milewski *et al.*, 1997]. Promising results on complex systems of practical importance have been obtained, including spectroscopy and photochemistry of different softwood kraft pulps [Sikorski *et al.*, 1999c; Wojciak *et al.*, 2000, 2002], and lignocellulosic materials [Wilkinson *et al.*, 1993a], radical reactions in cotton fabrics [Hunt *et al.*, 2002], spectroscopy and photochemistry of papers of historical interest [Wojciak *et al.*, 2003], and pyrene fluorescence quenching by halothane in poly(oxyethylene)–poly(oxypropylene)–poly(oxyethylene) triblock copolymers [Wen *et al.*, 1999].

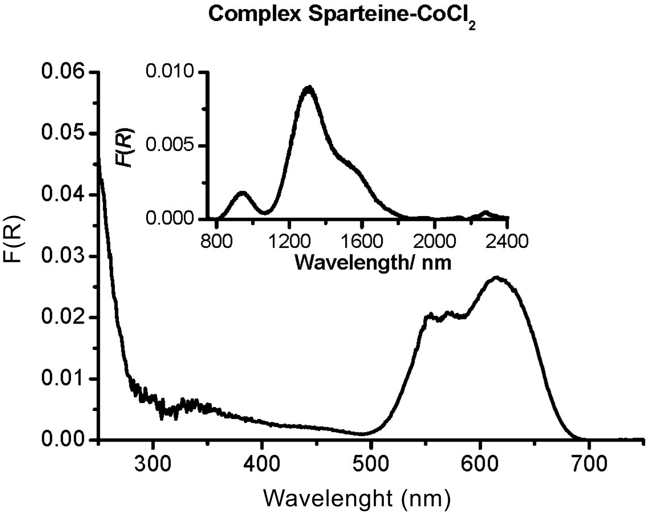

FIGURE 8. Ground–state diffuse reflectance absorption spectrum of (–)-sparteine-$CoCl_2$ complex.

Excellent review articles are available which highlight various possible ways in which solid support material can control the photochemistry of an adsorbed substrate, *e.g.* photochemistry of molecules adsorbed on zeolites [Bedja *et al*., 1994; Yoon, 1993], molecules adsorbed on SiO_2, γ-Al_2O_3, zeolites, and clays [Thomas, 1993], photochemistry on unreactive and reactive surfaces [Kamat, 1993], photochemistry of solid-state host-guest assemblies, with the use of cyclodextrins, inclusion clathrates, and zeolites [Ramamurthy & Eaton, 1994].

CONCLUSIONS

We demonstrated that diffuse reflectance spectroscopy of opaque samples can be successfully used for fundamental and applied studies, with minimum sample preparation Diffuse reflectance methods enable studying original foodstuffs without modification, and investigate their photodegradation mechanisms and kinetics in a controlled experimental environment. An interesting application is the capacity to evaluate frozen or solid foods remotely, without de-freezing them or taking samples for analysis; these techniques may be successfully used in the UV, visible and NIR spectral ranges. In particular, the diffuse reflectance flash photolysis techniques enable detection of transient species created by the light action in the real-world systems, which scatter light strongly and thus cannot be investigated by the traditional approach. The method has already proved its versatility in kinetic and mechanistic studies, and will find even more interesting and important applications in future. The diffuse reflectance methods also enable studies into the properties of photochemically inert matrices, using well-studied molecules as probes. Using such an approach, molecular mobility and microscopic diffusion coefficients can be evaluated. These parameters cannot be obtained by traditional macroscopic methods, but are essential for prediction of the thermal oxidation and photooxidation rates of foodstuffs.

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