Applications of Laser Techniques in Oils and Fats Analysis

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RINGKASAN

Kertas ini menghuraikan penggunaan teknik laser bagi tujuan menganalisis minyak dan lemak. Rangkai-kata 'teknik laser' didalam kertas ini bermaksud teknik-teknik dimana laser digunakan sebagai sumber irradiasi bagi mengkaji pendar fluor, serapan, reaksi fotokimia, sebaran cahaya, dan penderia jarak-jauh kimia. Potensi penggunaan teknik laser sangat luas dan amat bermanfaat.

INTRODUCTION

LASER, the acronym for *light amplification by stimulated emission of radiation,* was first introduced by the research physicist Theodore Maiman in 1960. However, due credit must be given to the great theoretical physicist, Albert Einstein for having formulated the basic principles and idea of the laser as early as 1916.

A comprehensive review of all laser applications is beyond the scope of this paper. This article concentrates only on the use of laser techniques in analysis of vegetable oils and fats. Emphasis is placed upon selected applications of lasers to analytical problems in palm oil. Extensive reviews on lasers and their applications can be extracted from Beesley (1976), Demtroder (1981), Hitz (1985), Radziemski *et al.* (1987), Omenetto (1979), Lee *et al.* (1984), Gagliano (1969) and Dovichi (1990).

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FUNDAMENTALS OF LASERS

Components of a Laser

Figure 1 is a schematic diagram of a typical laser source. A laser consists essentially of three components namely (i) the active lasing medium which amplifies an incident electromagnetic wave, (ii) the pumping source which selectively pumps energy into the active medium to populate selected levels and to achieve population inversion, and (iii) the optical resonator consisting of two opposite mirrors which store part of the induced emission concentrated within a few resonating modes. The lasing medium is the heart of the device and this may be a solid crystal (*e.g.* ruby), a semiconductor (*e.g.* gallium arsenide), a solution of an organic dye (*e.g.* rhodamine) or a gas (*e.g.* argon, helium etc.). The medium is activated or pumped by radiation from an external source such that a few photons of appropriate energy will trigger the formation of a cascade of photons of the

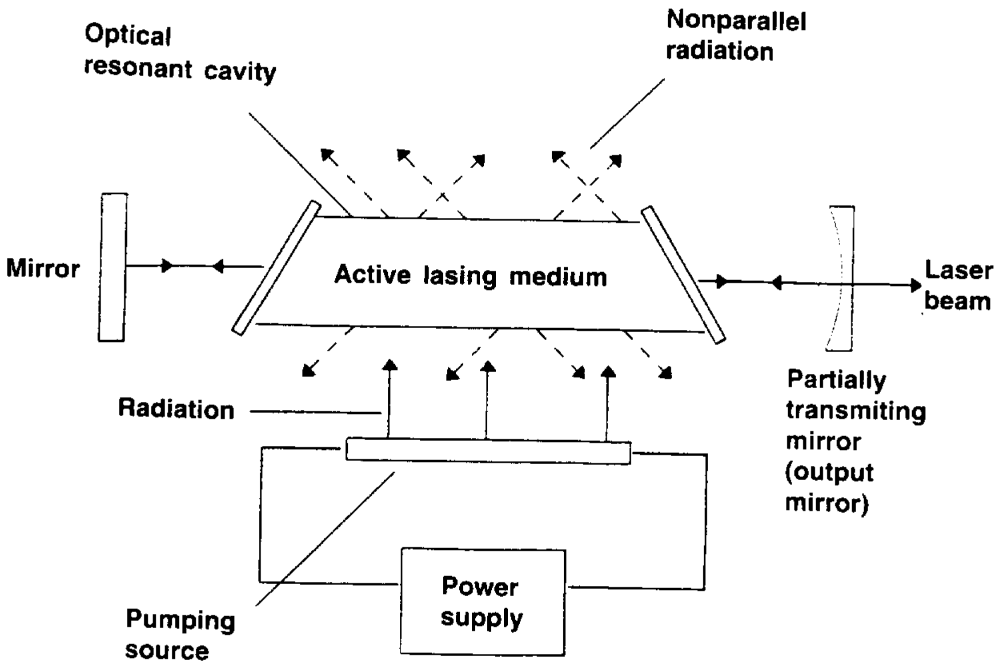

Figure 1. Schematic diagram of a typical laser source

same energy. In gas lasers, the power supply is connected to a pair of electrodes contained in a cell filled with the gas (*Figure 2*).

CHARACTERISTICS OF LASER LIGHT

Conventional light sources such as those from a fluorescent tube, electrical bulb or the sun are said to be incoherent. It is possible to make incoherent light sources coherent but at the great expense of intensity. It is the unique coherent property of laser which makes it such an important and powerful tool both in practical applications and fundamental scientific research.

The single descriptive term coherence is a combination of the characteristics of laser light which include monochromaticity and directionality together with phase consistency.

Monochromaticity

The light produced by a laser is monochromatic *i.e.* it is almost exactly the same colour. It is important to note the qualifying word 'almost' because even a laser does not give a perfectly pure colour because a perfectly monochromatic optical source would violate the uncertainty principle.[a]

[a]This principle holds that if you know (with no uncertainty) the wavelength of a source, you can know absolutely nothing about how long it has been on or how long it will stay on. The supposition is that it has been on forever and that it will remain forever a clearly impossible situation.

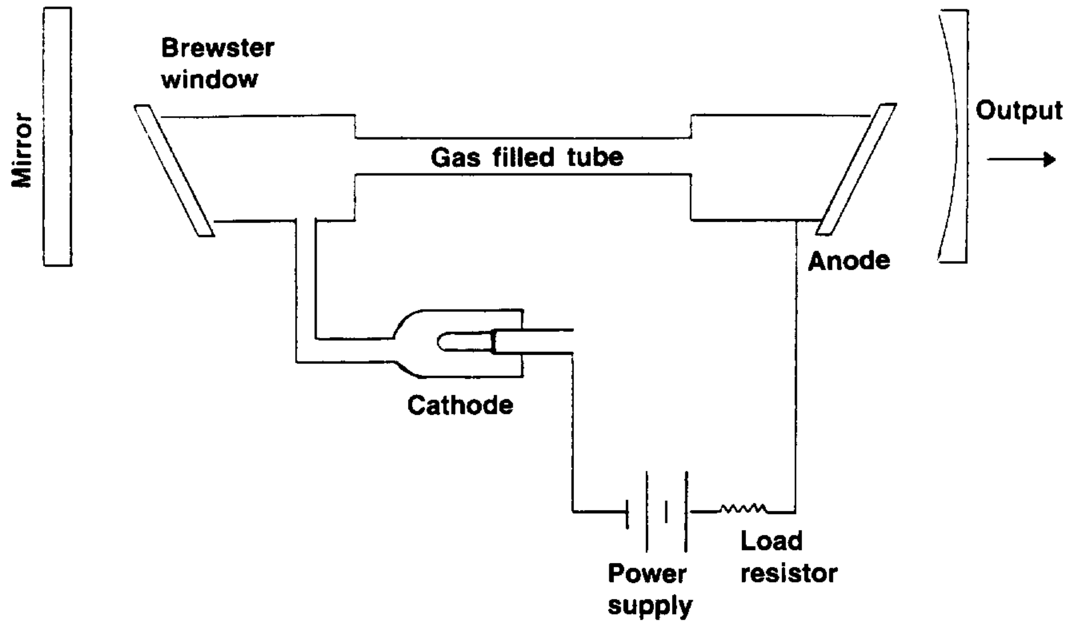

Figure 2. Schematic diagram of a low-power gas laser such as the helium-neon laser.

Directionality

Directionality is another unique property of laser light. All the light waves produced by a laser leave the laser in nearly the same direction. There is minimal divergence. This makes it possible to focus the laser beam onto a very small spot thereby increasing the intensity. Just as it is impossible to produce a perfectly monochromatic laser, it is also impossible to produce a perfectly nondiverging or collimated laser beam.

Coherence

The waves in a laser beam are almost of the same wavelength, the same direction and in the same phase. It is these three properties which make laser light coherent and which distinguish it from ordinary light sources. Laser light exhibits both spatial and temporal coherence. The former means that all the waves coming from the laser are in tandem. Temporal coherence occurs when the waves are emitted at even and accurately spaced intervals.

It is coherence which allows for the special applications of laser light. Highly directional laser light transports intense energy over large distances and phase consistent laser light provides holograms – all possible because of laser light coherence.

TYPE OF LASERS

The most commonly encountered laser is the red helium-neon (HeNe) laser. Its red light is seen in thousands of supermarket and departmental store check-out counters, in laser printers, in alignment tasks and in laboratory experiments.

Most lasers can be classified into one of the following categories – gas, solid state, semi-conductor, dye and excimer (*Table 1*).

Table 1 shows the chief wavelengths emitted by some common types of lasers and their applications. As shown in the table, the laser line might emit light at just one specific wavelength or many distinct wavelengths.

TABLE 1. SOME COMMON TYPES OF LASERS

Type	**Application**	**Wavelength emitted**	**Comments**
GAS LASERS			
Atomic lasers:			
Helium-Neon	Interferometry diffraction,		
Green	holography	543 nm	other lines
Yellow	alignment,	594 nm	at 1,152 and
Orange	Laser	612 nm	3391 nm
Red	fluorometry	632.8 nm	
Molecular lasers:			
Carbon dioxide	cutting, light knife in surgical cutting.	10.6 µm 337 nm	
Nitrogen	Laser fluorometry photochemistry	337 nm	
Excimer lasers:			193-35 nm
ArF	193 nm		
KrF	249 nm		
XeC1	308 nm		
XeF	350 nm		
Ar2	125 nm		
Kr2	146 nm		
Kr0	558 nm		
Metal vapour laser:			
Helium-Cadmium	Laser fluorometry	441.6 nm, 325 nm	

TABLE 1. (cont'd)

Type	Application	Wavelength emitted	Comments
Ion Lasers:			
Krypton (Kr)	Laser fluorometry, Raman spectroscopy, holography	476.2 nm, 520.8 nm 647.1 nm	multiline: 350-800 nm
Argon (Ar)	Laser fluorometry	488 nm, 514.5 nm	multiline: 351-528 nm
Ar-Kr	Holography, heating, diffraction spectroscopy, surgical instrument	568.2 nm, 647.1 nm	
SOLID STATE LASERS:			
Ruby (Cr: ruby)	drilling, vaporization, ranging scattering spect., pulsed holography LRMTS, welding, eye surgery	694.3 nm	
Neodymium (Nd) (Nd-YAG*, Nd: glass)	ranging, vaporization, communications	1.06 μm	
Alexandrite (Cr3+ doped into BeA1204)		700-800 nm	
Titanium: sapphire (Ti3+ doped into A1203)		670-1100 nm	
SEMICONDUCTOR LASER:			
Gallium-arsenide (GaAs)	laser communication, ranging	840 nm	
DYE LASERS:			
(Pumped by flashlamp or another laser)	Atomic flame fluorescence spectroscopy	Tunable	300 - 1,000 nm

**YAG - Yttrium aluminium garnate*
+LRMTS - Laser ranger and marked target seeker

LASERS IN CHEMICAL ANALYSIS

The high power, directionality, purity of colour, temporal and spatial coherence of the laser has made it an indispensable analytical tool. The laser can be employed in the study of how chemical reactions occur, to initiate and control chemical reactions and to detect ultra trace levels of chemical components embedded in their 'real' or natural matrices (Brumer, 1989; Zare, 1984). The dramatic impact of laser in chemical analysis can be seen by the impressive number of publications in this area, one of the most important of which is in the field of laser spectroscopy. (Demtroder, 1981; Radziemski *et al.*, 1987).

Laser Spectrochemical Analysis

The laser has set new standards in spectroscopic detection. This ideal spectral source is used as a stable source of radiant energy in high resolution spectroscopy such as Raman spectroscopy, molecular absorption spectroscopy, emission spectroscopy and Fourier Transform IR spectroscopy. The earlier limitation of lasers in spectroscopy was that the radiation from a given laser source was confined to the few discrete wavelengths of the particular laser in use (*Table 1*). Today dye lasers have made it possible to tune these sources to obtain a narrow band of radiation at any chosen wavelength within the range of the source. A general guide to various laser uses in *Table 1*, gives an idea of the wide ranging applications of lasers in spectroscopy, industry, medicine and engineering.

Laser Photochemistry

This is a branch of physical chemistry where chemical reactions are induced, altered, monitored or controlled by laser irradiation. Lasers have been successfully used to drive chemical reactions in the study of single-collision chemical dynamics. Ultrashort laser pulses are used to probe the reaction dynamics of very fast processes because photochemists now have a tool to manipulate the pathway of chemical processes. Extremely intense lasers can now be used to induce dissociation of a specific bond in a molecule. Another important usage is in the separation of isotopes. Since the laser preferentially dissociates molecules of a particular isotope, the isotopically enriched fragments which react with added scavengers can be removed. This technique is applied to the separation of isotopes of sulphur, nitrogen, boron and hydrogen.

POSSIBLE APPLICATIONS OF LASER TECHNIQUES IN OILS AND FATS ANALYSIS

Table 2 is a summary of the potential uses of lasers in analysis of oils and fats. Clearly, before lasers can be successfully applied to analytical problems of oils and fats, the absorption spectra of the sample under investigation have to be known. In the case of vegetable oils and fats, the absorption spectra are affected by a myriad of components which make up the complex oil matrix. For example, the crude palm oil absorption spectrum shows absorbance in the 400–500nm region and, depending upon the degree of fruit ripeness, absorbance

TABLE 2. POSSIBLE APPLICATIONS OF LASER TECHNIQUES IN OILS AND FATS ANALYSIS

Laser Technique/Field	Compounds which can be determined/monitored
1. Laser-Induced Fluorescence	– pigments such as carotenoids, chlorophylls, anthocyanins, xanthophylls. – Antioxidants both natural and synthetic *e.g.* tocopherols tocotrienols, BHT, BHQ. – Sterols *e.g.* cholesterol. – contaminants *e.g.* aflatoxins, polyaromatic hydrocarbons (PAHs), pesticide residues. – Enzymes *e.g.* lipase. – Effluent water. – Phospholipids, inorganic phosphates. – Other minor components by doping with a fluorophore *e.g.* carbonyls. – Triglycerides.
2. Laser Absorption	
• Chemical-concentration monitoring	– Oxidation products in oil *e.g.* aldehydes, dienes, trienes.
• Chemical-Reaction Diagnostics	– Kinetics of oxidation. Kinetics of crystallization. *e.g.* rate of crystallization.
• Chemical-Processing Control	– Fractionation process – On-line monitoring of refining process.
3. Laser Photochemistry	– Enhancing/catalyzing specific chemical reactions by selective excitation of reacting components in oil *e.g.* hydrogenation, bleaching. – To monitor oxidation pathways and intermediate states.
4. Laser nephelometry	– study of the crystallization process. – cloud point and melting point
5. Laser Remote Sensing Techniques	– Pollution monitoring of atmosphere at palm oil mills *e.g.* CO content. – Monitoring of effluent. – Monitoring oil loss during milling.

may be observed in the 650–680 nm region. Added to that, solvents and a variety of contaminants also contribute to the final absorption spectrum. The distinct advantage of using lasers as excitation sources for spectral analysis of oils and fats is that the technique can not only improve detection of trace substances but also pick-up the presence of these trace components embedded in their original oil matrix. This dispenses with most pre-extraction steps or solvent dilution which are usually required in conventional spectroscopic studies. Thus a more accurate analysis is obtained because ultra trace levels of analyte need not be lost or diluted in long, tedious preparative steps. The ability of analyzing compounds in their real matrices also gives the analyst more accurate information on the composition of components in oils and fats. Analyses are now possible in practical situations where matrix interference have often, in the past, proved to be the real limiting factor in trace analyses.

Laser Induced Fluorescence (LIF) Spectroscopy

In order to fluoresce, a molecule in the ground state must absorb energy from a source of electromagnetic or chemical energy and be raised to a higher energy singlet state. When the molecule drops from the singlet state back to its normal ground state, much of the absorbed energy is emitted as fluorescence. The emitted wavelength is always longer (less energy) than that of the absorbed energy (White *et al.*, 1970; Guilbault, 1973). Many compounds and elements exhibit this fluorescence property.

The quantitative relationship between fluorescent intensity (I_f) and concentration is given by:

$$I_f = O_f\, I_o\, [1 - \exp(-ebc)] \qquad (1)$$

where O_f is the fraction of incident ray which is re-emitted as fluorescence (or the quantum yield of fluorescence), I_o is the incident power of the exciting beam, e is the molar absorptivity of the species under study, b is the sample cell pathlength, and c is the molar concentration of the fluorophore. For dilute solutions, Equation 1 reduces to

$$I_f = KO_fI_oebc \qquad (2)$$

where K is an instrumental factor.

Equation 2 indicates that fluorescence intensity depends on molar absorptivity, quantum yield, collection efficiency of the instrument and intensity of excitation. Of these variables, excitation intensity is the easiest to increase. The unique spectral properties of the laser light make it an ideal excitation source in laser-based fluorometry (Bright, 1988).

Although not all compounds in oils and fats fluoresce, the significant few which do, make laser fluorometry an important and selective technique in their detection. Added to this, non-fluorescing species may be derivatised to fluorescing compounds by incorporating a fluorescence tag (Patonay *et al.*, 1991). Since the signal to noise (S/N) ratio of fluorescence is far superior to Ultraviolet (UV) and visible absorbance, the ability to detect ultra trace levels of important minor components in oils is promising. *Table 2* suggests that LIF can be investigated for the detection of both minor and major components in oils and fats from pigments, antioxidants, sterols, phospholipids, triglycerides, enzymes to contaminants such as aflatoxins, polyaromatic hydrocarbons (PAHs) and pesticide residues. Since all water samples, except those of the highest purity, fluoresce when exposed to UV radiation, 'blue' water fluorescence has been used to study water quality. The quality monitoring of effluent from the pulp and paper industry was a subject of such study by LIF (Winefordner, 1978). Perhaps the effluent from palm oil mills can also be similarly investigated by LIF techniques.

A typical LIF experimental set-up is shown in *Figure 3*. Similar systems have been used by researchers at the University of Malaya to determine palm fruit ripeness (Wong, 1988) and the Palm Oil Research Institute of Malaysia (PORIM) to detect chlorophylls in crude vegetable oils (Tan *et al.*, 1993a, 1993b).

Laser Absorption Spectroscopy

Previously, one of the main disadvantages of laser absorption applications was the lack of conveniently tunable commercial lasers in some spectral ranges. Presently, the whole spectrum between 100 nm to 1000 µm can be tuned by non-linear frequency mixing techniques. In conventional spectroscopy, the spectral resolution is substantially limited by the equipment used, particularly the intensity and spectral purity of the light source. Using a laser, one can do away with extra dispersive devices such as the monochromator because the laser itself acts as a monochromator. The result is an im-

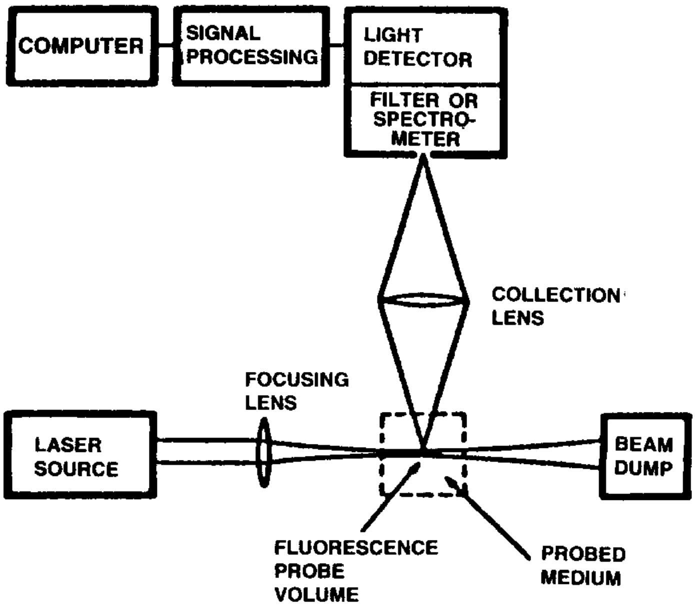

Figure 3. Schematic diagram of a typical laser-induced fluorescence experiment.

provement of spectral resolution 1×10^4 to 1×10^{15} times higher than conventional absorption techniques. Thus laser spectroscopy can be used to enhance the present absorption methods for studying oxidation products in oils, to look into the kinetics of both oxidation and crystallization and perhaps even to monitor both the refining and fractionation process of oils.

Laser Photochemistry

Controlling chemical reactions by using lasers, termed coherent control, is an exciting new field of chemistry. The concepts underlying coherence chemistry are well accounted by Brumer, 1989.

Lasers can also be used to probe chemical reactions of oils and fats. They can be used to enhance or catalyse specific chemical reactions in the investigation of reactions such as bleaching or hydrogenation. Laser irradiation can selectively affect the desorption-adsorption process to enhance catalytic reactions in these two surface chemical reactions. Another potential area of application is the study of the interaction of intense laser light with oil. This can be used to monitor oxidation pathways and intermediate states of chemical reactions or as an alternative method for conventional accelerated oxidative test like the rancimat, AOM or swift test.

Laser Nephelometry

The measurement of amplitude, phase, frequency and direction of scattered laser light from objects is a non-intrusive and non-destructive way of gathering information about the objects. Both Rayleigh and Mie Scattering of laser light can be applied, depending upon the particle size under study. Thus laser nephelometry can be useful in the investigation of the palm oil crystallization process and to enhance the sensitivity of present methods for cloud point and slip melting point determination of vegetable oils and fats.

Laser Remote Sensing Techniques

Two of the most pressing issues in our world today are that of atmospheric and environmental pollution. The study of atmospheric pollutants is of great urgency since industrial air pollution is now an extremely serious problem. Laser remote sensing is a technique using lasers to measure properties of a medium which is situated at some distance from a laser system. It has been successfully used for remote measuring of atmospheric pollutants and bodies of water. The advantages of laser remote sensing lie in its ability to (i) probe regions inaccessible to point analysis (*e.g.* molecules in atmosphere) (ii) to rapidly probe a large area or volume as in the measurement of sulphur dioxide in the effluent plume from power plants, and (iii) to measure concentrations and distribution *in situ* (without sampling). Laser remote sensing can be used to monitor the atmosphere around palm oil mills, to check the quality of palm oil mill effluent and probably to measure oil loss during milling.

Laser Instrumentation

For laser techniques to be widely accepted, the instrumentation must be sufficiently rugged and simple to use by a technician. The laser system must also be relatively inexpensive. Fortunately, recent technological advances have produced fairly low costs, reliable and rugged lasers for laser-based instrumentation in chemical analysis. The development of several new tunable solid-state lasers, which operate without the use of toxic organic dyes, have made lasers even more indispensable in spectrochemical research (Andrews, 1991). Although the dye laser is likely to remain the major source of tunable radiation, the solid-state lasers are viewed as ideal replacements in the near future. Current research is directed to the development and marketing of laser diagnostic techniques with their complementing instrumentation for numerous routine chemical analyses (McCoustra, 1991).

CONCLUSION

The laser beam is highly monochromatic, directional and spatially and temporally coherent. All applications of lasers are dependent upon one or more of these four unique spectral properties. The laser presents a non-intrusive and non-destructive manner of probing chemical species because of its extremely short pulse of intense light. When the laser was first invented in 1960, it was described as 'a solution in search of a problem'. Today, lasers have proved to be the solutions to many problems. It has been demonstrated that lasers are much better and faster than more conventional techniques. In chemical analyses, laser application is a combination of chemical and instrumental technologies to enhance basic methodologies in high sensitivity analysis of complex systems such as oils and fats. Certainly the potential applications of lasers for oils and fats analysis presented in this paper are far from complete but it serves to illustrate the impact of lasers on the development of innovative diagnostic techniques.

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