CCD	charge c
CW	continu
DFWM	degener
DIAL	differen
FT-ICR	Fourier resonan
FTIR	Fourier
ICP-AES	inductiv atomic e
ICP-MS	inductiv

CHEMICAL
SOCIETY
REVIEWS

Laser techniques for chemical analysis

Richard Snook

Department of Instrumentation and Analytical Science, University of Manchester Institute of Science and Technology, PO Box 88, Manchester, UK M60 1QD

In this review a wide range of laser-based techniques for chemical analysis is discussed with reference to the principles and practical utilities of each technique. Thus techniques for atomic spectrometry, elemental analysis, molecular spectrometry, LIDAR, photothermal spectrometry and mass spectrometry are considered. Where possible qualitative comparisons are made with alternatives for particular analyses, *e.g.* atomic absorption and emission spectrometry. Where alternatives do not exist *e.g* LIDAR, the practical utility and applications of such techniques are discussed.

1 Introduction

During the first two decades since the invention of the ruby laser in 1963 it was fashionable to say that lasers were 'solutions looking for a problem', and this was especially true in spectrochemical analysis where most advances were being made in analysis techniques such as inductively coupled plasma atomic emission and atomic absorption spectrometry, Fourier transform infra-red spectrometry, microwave spectrometry, and photoacoustic spectrometry. The driving force for the development of these analytical techniques was the requirement to carry out precise and accurate determinations with good detection limits and reliability for a variety of elements or compounds in several different types of sample. In this respect the expense and temperamental nature of laser sources, sometimes restricted to a few analytical wavelengths, militated against their use and to some extent still does.

Nevertheless, in recent years many interesting and potentially useful analytical techniques have emerged which utilise laser sources. Some are truly spectroscopic in which the laser is used as a source of photons for absorption, or fluorescence or non-linear spectroscopies whilst in others the laser is used as a sampling aid simply to blast off atoms, molecules or particles from a sample or substrate into a separate analysing instrument, *e.g.* an inductively coupled plasma or a mass spectrometer. Indeed in several of the techniques described in this review the laser cannot be regarded as a solution to a problem, rather the laser source has generated completely new diagnostic or analytical techniques with their own attendant problems.

Richard Snook is Professor of Analytical Science at the University of Manchester Institute of Science and Technology (UMIST) in the UK. He is currently Head of the Department of Instrumentation and Analytical Science. He received his PhD degree in Atomic Spectrometry from Imperial College, London in 1977 where he continued to work in the field of inductively coupled plasmas for emission spectrometry, chemical sensors and atomic absorption spectrometry. Since moving to Manchester in 1986, he has continued to pursue research in these areas and at the same time has established a thriving Research Group in Photothermal Laser Spectroscopy. He received the Silver Medal of the Royal Society of Chemistry Analytical Division in 1989 and the DSc of the University of London in 1995 in recognition of his research in Analytical Science.

It is the aim of this review to consider the significance of these techniques in the context of chemical analysis. The emphasis will be more on the principles, practice and potential utility of such techniques rather than detailed discussion of the instrumentation required. This approach is consistent with the required length and tutorial nature of the review. Fortunately, there are several reviews and texts dealing with laser sources and of these the reader is directed towards the brief review of McCoustra in *Laser Spectroscopy*, edited by Andrews and Demidov,[1] or alternatively if a deeper understanding is required the text of Hecht.[2] Although a detailed discussion of lasers is to be avoided it is important that their useful features are recognised in the context of spectrochemical analysis and hence these sources are discussed in general below and in the text when related to specific techniques.

Those parameters which make lasers excellent sources for spectrometry are:

(*i*) intensity or power;
(*ii*) wavelength monochromaticity (for atomic spectrometry);
(*iii*) tunability (for molecular spectrometry);
(*iv*) coherence length and time;
(*v*) propagation range.

Lasers can be operated in either the continuous wave mode (CW) or pulsed mode, or either depending on the lasing medium and pumping mechanism. Many early laser types, *e.g.* ion lasers and Nd^{3+}YAG lasers, produce discrete laser wavelengths and as such are not generally useful for spectrometry unless the chemical system under study coincidentally absorbs at the particular wavelength of the laser. True laser spectrochemical analysis came about with the introduction of tunable laser sources, for example the dye laser, which is pumped by either an ion laser or excimer laser. Dye lasers produce wavelengths over a 50–100 nm range in the UV, visible and near infra-red regions of the electromagnetic spectrum. The exact location of the centre wavelength depends of course upon the fluorescence properties of the organic dye chosen as the lasing material. A popular choice of pump laser is the 308 nm exciplex laser which can be used to produce dye laser output pulse energies of up to 500 mJ per pulse.

In the near infra-red the pumped Ti–sapphire laser can be used to produce continuously tunable radiation in the wavelength range 700–1100 nm. Frequency doubling techniques can be used to extend the wavelength range of both dye and Ti–sapphire lasers deeper into the UV region. Of particular note in this respect are the non-linear optical methods of second harmonic operation and sum-frequency generation. Much interest is currently focused on the use of β-phase barium borate (BBO) as a non-linear crystal to produce optical parametric oscillators (OPO) with tunable radiation over the wavelength range 200–400 nm. Typically, such an OPO would be pumped by an Nd^{3+} : YAG laser and the wavelength range is obtained by doubling and sum frequency generation. Diode lasers made from Group III/V semiconductor elements of the periodic table have band gaps which are sufficient for photon emission in the spectral region from 600 nm–2 μm. Thus, a series of diode lasers are available in this region.

In the infra-red, lasers are normally molecular gas lasers or diode lasers. Of the molecular gas lasers the CO_2 laser is commonplace and well known to IR spectroscopists. The lasing medium is CO_2 and produces radiation by transitions between vibration rotational levels in the spectral region 9.6–10.6 μm in a series of narrow closely spaced lines giving a degree of tunability, although not continuous, across this region at powers of a few hundred watts (cW) or a few Joules (pulsed). Other important molecular gas lasers are the CO laser (5.0–6.5 μm) and the N_2O laser (10.3–11.1 μm) which operate only in CW mode. Far infra-red lasers (> 30 μm) are normally based upon optical pumping of simple organic molecular gases such as methanol (CH_3OH), methylamine (CH_3NH_2) and formic acid (HCOOH). Typically, these media are pumped using narrow bandwidth CO_2, CO or N_2O lasers which results in several discrete output wavelengths. Thus, methanol as a lasing medium produces a series of lines at 70.6, 96.5, 118.8, 163.0, 570.5 and 699.5 μm. Diode lasers can also be fabricated from elements in groups IVb and VI of the periodic table giving rise to the so-called lead salt diode lasers (*e.g.* $PbS_{1-x}Se_x$; $Pb_{1-x}Sn_xTe$; $Pb_{1-x}Sn_xSe$) in which band gaps are sufficiently small to yield photon emission between 3 and 27 μm. Again tuning over a range of 50 cm^{-1} is achievable using current and temperature programming techniques. For convenience the operating parameters of commonly used lasers are summarised in Table 1.

The mode of operation and particular features of operation of a laser source which are attractive to spectroscopists also depend upon the chemical analysis technique employed. Thus, CW tunable lasers are useful for studying equilibrium processes in absorption or photothermal processes whereas pulsed lasers are useful for time-resolved studies, *e.g.* of excited state lifetimes. High power and normally pulsed techniques are required to perform remote detection (LIDAR), laser induced breakdown spectrometry (LIBS) or matrix assisted laser desorption mass spectrometry (MALDI-MS). Narrow linewidths may also be important, especially in atomic spectrometric techniques, whereas coherence length and time might be important for certain non-linear techniques for example degenerate four-wave mixing (DFWM) and coherent anti-Stokes Raman spectroscopy (CARS). Indeed many of the techniques described in this review would simply not be possible without the use of lasers with their unique properties as light sources.

The field of laser spectroscopy is very broad and necessarily not all aspects can be covered in this review. Those techniques chosen below are either established in chemical analysis or in my view could be developed into practical analytical systems offering potential advantages over existing techniques. Many, but not all, of these diagnostic techniques have therefore been omitted, *e.g.* the use of lasers to study photofragmentation has been left out but degenerate four-wave mixing has been left in as it could conceivably be developed into a general analytical technique for elemental analysis.

Each of the subject areas discussed are worthy of a review in their own right and indeed reviews in these subjects are available and referenced in appropriate sections below. Detailed discussion of extensive subjects such as Raman spectrometry and LIDAR will not be undertaken for this reason.

2 Atomic spectroscopy and elemental analysis

Atomic techniques require narrow line widths of the order 0.002–0.02 nm to match atomic line widths associated with absorption of electromagnetic radiation at flame or furnace temperatures. Often lasers such as ion or Nd : YAG pumped dye pulsed lasers are used delivering powers of typically 1 J per

Table 1 Common laser sources

Laser material	Mode of operation	Wavelength	CW Power or Pulse (W) Energy (J)
UV–VIS near IR			
He-Cd	CW	325; 441.6 nm	< 50 mW
Tm^{3+} : YAG	CW	1870–2160 nm	< 1 W
CO^{2+} : MgF_2	Pulsed	1750–2500 nm	< 75 mJ
Pumped Cr^{3+} : Mg_2SiO_4	Pulsed/CW Average	1167–1345 nm	< 250 mW
Pumped Ti^{3+} : Al_2O_3	CW	660–1180 nm	< 2 W
Argon Ion (Ar^+)	CW	514.5 nm	< 25 W
Krypton Ion (Kr^+)	CW	647 nm	< 6 W
Nitrogen	Pulsed	337 nm	< 1.0 mJ
Excimer	Pulsed	308 nm	< 500 mJ
XeCl		351 nm	< 1 J
Nd^{3+} : YAG	Mode Locked (Average CW) or Pulsed	1064 nm (doubled or tripled)	< 1500 W
		532 nm	< 200 mJ
		355 nm	
Cu vapour	Pulsed	510.5 nm	< 1 mJ
		578.2 nm	
Exciplex pumped dye lasers	Pulsed	300–1000 nm Using different dyes	< 10 mJ
Ion laser pumped dye lasers	CW	400–700 nm	< 1 W
UV pumped optical parametric oscillator (OPO)	Pulsed	400–700 nm (signal)	70 mJ
		700–2000 nm (idler)	10 mJ
		200–400 nm (doubling and scan frequency)	35 mJ
Diode lasers In Ga Al P Ga Al As In GaAs	CW	630–980 nm at discrete frequencies	< 150 mW Single 50 W Arrays
IR			
CO_2	CW/Pulsed	9.6–10.6 μm	CW < 200 W Pulsed 2 J
CO	CW	5.0–6.5 μm	< 1 W
N_2O	CW	10.3–11.1 μm	< 20 W

pulse. To achieve the desired linewidth it is necessary to employ an additional wavelength narrowing device such as an etalon in the dye/laser cavity and frequency doubling techniques to access wavelengths in the region 200–400 nm which is an important region of the spectrum for both atomic and molecular spectrometry.

Techniques which require narrow line widths, which are often power-dependent are:

(*i*) laser enhanced atomic fluorescence;
(*ii*) laser enhanced ionisation spectrometry;
(*iii*) laser resonance ionisation spectrometry;
(*iv*) degenerate four-wave mixing;
(*v*) laser induced breakdown spectrometry.

In all but the last of these techniques the laser is used to pump specific transitions in an atomic vapour produced in a separate atom cell or source. In the last technique a laser pulse is used to atomise, excite and ionise a solid, liquid or gaseous medium producing a laser plume from which atomic emission can be observed.

Laser enhanced atomic fluorescence[3] (LEAFS) is a technique in which excited state atomic fluorescence is observed after photon absorption and excitation. Quantitative concentration measurements can be made provided that the upper level is not saturated by too high a laser power. When this condition is met then the total fluorescent intensity I_F is given by eqn. (1),

$$I_F \propto N_0 \, B_{02} \, \Phi \, I_{\text{laser}} \qquad (1)$$

where N_0 is the number density of initial states undergoing excitation, B_{02} is the Einstein transition coefficient for absorption and ϕ is the fluorescence quantum yield for the excited state.

If the upper state is saturated by using higher laser powers then the fluorescence signal becomes independent of quantum efficiency because the source induced radiative excitation and de-excitation rate coefficients dominate the excitation mechanism. In effect at high powers the fluorescence signal is independent of the source intensity but dependent on the concentration of analyte species in the source. The normal LEAFS technique[4] is derived from Stokes fluorescence, to minimise scattered source radiation contributing to the signal and noise at the detector as would be observed with measurements of direct line fluorescence.

In principle very high detection powers are achievable with LEAFS and indeed work by Winefordner *et al.*[5] demonstrated this capability by the detection of femtogram quantities of lead atomised from a graphite furnace. In this paper the authors employed a 9 kHz copper vapour laser to excite lead at a wavelength 283.3 nm in dilute whole blood samples. Using background correction techniques the absolute detection limit was found to be 10 fg cm^{-3} (an absolute limit of 100 ag). The sensitivity of LEAFS has also proved valuable for measurements in regions where environmental pollutant levels are extremely low. For example Bolshov *et al.*[6] have used LEAFS routinely for the determination of Pb and Cd at sub pg cm^{-3} levels in Antarctic and Greenland snow. The results obtained agree well with those acquired by isotope dilution techniques and also provided detection limits of 0.18 and 0.07 pg cm^{-3} for Pb and Cd, respectively.

Such extreme sensitivity is a consequence of atomic fluorescence being essentially a source background free technique which is also source power dependent provided optical saturation is avoided. Selectivity is enhanced because of the use of an element specific excitation step and fluorescence step defined by the unique energy levels of each element.

It could be argued that such detection power may well be significant as required levels of detection are pushed beyond the limits of conventional graphite furnace AAS as a consequence of environmental legislation. The wisdom of ever more stringent detection requirements must be questioned however, given the ubiquitous nature of many elements at the ultra trace level. It is difficult to imagine the stringent requirements of sample preparation to achieve routine and meaningful analysis at these levels.

Ionisation of an atomic vapour can be utilised for elemental analysis in the technique of *laser enhanced ionisation spectrometry* (LEIS) in which a laser source, normally a pulsed Nd:YAG or XeCl excimer dye laser, is used to selectively excite an analyte transition to produce ions. The analyte atomic population is produced in an atom cell, normally a flame or graphite furnace. Laser induced excited states are further excited by collisions resulting in an increase in the number of ions and electrons in the flame which can be measured by applying an electric field to the flame *via* two electrodes and measuring a change in current as the electron density changes. The electrodes are normally placed either side of the flame and in some configurations a water cooled cathode is actually placed in the flame to measure changes in current with an applied voltage of *ca.* 2 kV. A complete discussion of the technique, theoretical principles and analytical applications can be found in the excellent monograph of Travis and Turk.[7]

A detailed study of collisional ionisation and photoionisation rates in LEIS has been carried out by Omenetto *et al.*[8] in which a fluorescence dip technique was used to quantify ionisation rates of excited state manganese atoms in an oxygen–argon–acetylene flame. These authors derived expressions for ionisation rates and quantum and ion yields in a comprehensive treatment which has enhanced the theoretical understanding of the technique and demonstrated its use as a diagnostic tool in spectrochemical measurements.

Laser resonance ionisation spectrometry (LRIS) is similar to LEIS but in this case a second laser frequency is used to ionise a selectively laser excited transition. In effect the process is photoionisation from an excited atomic state. The detection method can be the same as used in LEIS with flames or furnaces used as atom cells. *Resonance ionisation mass spectrometry* (RIMS) is an alternative detection method which offers great sensitivity.[9] In this technique separate lasers are used to produce an atomic sample from a substrate and to ionise those neutral atoms or molecules thus making their separation by mass spectrometry possible. RIMS is a relatively recent technique which can be used for the ionisation of most of the elements of the periodic table using multiphoton ionisation in which successively higher energy levels can be excited using a combination of laser frequencies until ionisation is achieved. In practice this can result in a rather unwieldy and very expensive piece of equipment. For example to cover most of the periodic table would require several lasers and frequency doubling crystals.[10] It is perhaps this complexity and expense of equipment which militates against the widespread use of such techniques for elemental analysis when compared to the ease with which the same information can be obtained with equal sensitivity from for example inductively coupled plasma mass spectrometry! Perhaps one advantage over other elemental techniques is that point sampling of a surface can be achieved as reported by Arlinghams *et al.*[11] who developed the technique of *laser ablation resonant ionisation spectrometry* (LARIS), although this is also true of secondary ion mass spectrometry (SIMS). Nevertheless laser mass spectrometry methods have made significant contributions to the determination of molecular and biological materials which are discussed later in the review under matrix-assisted laser desorption and ionisation mass spectrometry.

Laser desorption and excitation is also embodied in the technique of *laser induced breakdown spectrometry* (LIBS) which is a comparatively recent technique in which a powerful pulsed laser is used to excite atomic emission in a gas or liquid. In the case of solids the laser pulse serves also to ablate and atomise the sample. In early experiments to generate laser sparks in a liquid Cremers *et al.*[12] demonstrated the feasibility of this approach using a 45 mJ per pulse focused Nd:YAG laser with a pulse duration of 15 ns. It was necessary to use a time resolved measurement with signal averaging to extract useful signals for Na, Li, K, Rb, Cs, Be, Mg, Ca and Al. The spectral features observed after the initial scattered pulse comprised a spectrally broad continuum emission and features due to singly ionised and neutral atom emission. Time resolution is required as the relative intensities of these change (*i.e.* spectral colour shifts) with respect to each other as the plasma spark cools. For example the disappearance of Ca^{II} ionic emission and the appearance of Ca^{I} emission occurs between 100 and 400 ns after the pulse maximum emission and at times greater than 1 μs Ca^{I} and CaOH emission dominates. Time resolved studies of aerosols by Radziemski *et al.*[13] clearly show this time dependence for nitrogen and oxygen in aerosols again using a Nd : YAG laser of pulse energy 50–300 mJ and pulse duration of 20–80 ns.

Recent applications of the LIBS technique have included rapid screening of trace heavy metals (Cd, Cu, Cr, Ni, Pd and Zn) in soils[14,15] with detection limits reported to be better than required regulatory limits. These authors note that matrix effects for example water and fibre content must also be considered when optimising the LIBS procedure. In principle the technique can also be applied to gaseous samples and indeed such a system has been proposed for the quantitative determination of pollutant concentrations in air.[16] Thus LIBS and *time resolved laser induced breakdown spectrometry* (TRELIBS) appear to be applicable to a wide variety of sample types. These techniques cannot be considered as routine however owing to the still uninvestigated potential matrix effects, the requirement for a better understanding of the laser pulse–substrate interactions, the difficulty of calibrating the technique, and of course the expense and complexity of instrumentation. Nevertheless the concept of putting the spark or plasma into the sample rather than the sample into a plasma or spark as in conventional AES does have some philosophical appeal if only to avoid the vagaries of sample introduction systems. Work in this area could be fruitful and have spin-offs, especially in solid sample LIBS for other ablative techniques, *e.g.* LARIS and RIMS as described above in which a laser is used to create a surface plasma of neutrals and ions for detection by mass spectrometry.

Lasers are also frequently used as sampling devices for atomic spectrometry, for example *laser ablation inductively coupled plasma atomic emission spectrometry* (LA–ICP–AES)[17] is well established in the analysis of geological materials. The sample is subjected to a pulse of laser energy through a microscope objective typically delivering fluences of greater than 10^9 W cm^{-2} to the surface of the sample. The spot size at the surface is *ca.* 20–100 μm and the resulting pit arising from the ablation of material can be a few hundred μm deep. Ablated material is then passed to the ICP where atomic emission is observed. In this way direct analysis of solid materials is facilitated avoiding contamination and dilution errors sometimes associated with aggressive sample dissolution procedures used to dissolve, for example, geological materials. Also detection limits are improved by avoiding dilution through the dissolution process. A potential disadvantage of such solid sampling, however, arises if the sample is not homogeneous in that the ablation process yields point information and hence the analysis is not representative of the bulk material. In some circumstances however this might be considered an advantage if such point information was actually required. Laser ablation is a particularly attractive sample introduction technique for ICP mass spectrometry (ICP-MS) as the sample is introduced as a dry aerosol thus avoiding some of the molecular ion mass interferences caused by the combination of argon with oxygen, hydrogen and hydroxyl species formed from introduction of wet aerosols by solution nebulisation. Given the superb sensitivity of ICP-MS combined with the advantages of solid sampling, laser ablation ICP-MS has great potential in many areas of analysis, where detection limits are of paramount importance, *e.g.* semiconductor materials and environmental analysis.

So far emission and mass spectra have been considered but it is worth observing that a laser is an ideal source for atomic absorption where the requirement for monochromatic radiation is normally met using hollow cathode lamps. Clearly, the use of narrow linewidth tunable dye lasers as a replacement for hollow cathode lamps would not be justifiable from an expense point of view. However, with the introduction of tunable diode lasers the possibility of laser atomic absorption spectrometry for routine analysis is brought closer to reality, yet still restricted owing to the lack of such devices in the UV region and blue region of the spectrum, where many elemental resonance lines lie. The only practical way of accessing these regions with semiconductor diode lasers is to employ frequency doubling techniques and then the expense argument weighs heavily against the technique when compared to the use of hollow cathode lamps. Nevertheless, Niemax *et al.*[18] have demonstrated the use of a semiconductor diode laser for the determination of rubidium at the ng cm^{-3} level using graphite furnace atomisation. Niemax has also postulated the use of several tunable diode lasers to cover a wider spectral range.

Degenerate four wave mixing[19] (DFWM) is a non-linear technique in which three beams of degenerate frequency are mixed in a non-linear medium, *e.g.* an assembly of absorbing atoms in a flame of plasma. A forward pump beam, I_F is incident on the non-linear medium and counter propagating to this is a backwards pump beam I_B. The laser is also used to produce a probe beam (I_p). Beams I_F, I_B and I_p induce electrical polarisation which oscillates at $\omega_{pc} = \omega_f + \omega_p - \omega_B$ in the direction $K_{pc} = (K_f + K_p - K_B)$ where the subscript pc refers to the phase conjugate beam the wave vector of which is reversed compared to the probe beam K_p. In effect when the degenerate frequency is at the absorption wavelength of the atomic species in the atom cell an effective grating is formed in the atomic vapour by interference between I_f and I_B which is probed by I_p. The intensity of the backward propagating phase conjugate beam I_{pc} can be written as eqn. (2), where A is the

$$I_{pc} = \frac{[A \ln 10]^2 \, I_p}{4\,(3+\delta^2)^3} \qquad (2)$$

absorbance of the atomic population and δ is a detuning parameter. Thus, as the absorbance changes I_{pc} changes *via* the absorbance term. Also as the frequency of the laser is scanned across the absorption line width then I_{pc} varies according to the line profile thus providing a high resolution, Doppler free measurement of the linewidth without a conventional spectrometer. Although it is difficult to envisage a practical DFWM device for routine chemical analysis the technique has found applications in many diagnostic aspects of atomic spectrometry, and more recently in molecular spectrometry as a detector for capillary column chromatography.[20] The advantage perceived over conventional UV detection is that, theoretically, a signal is observed over a dark background as a result of light absorption which should yield very low detection limits. In practice thermal lensing of solvents reduces mixing efficiencies of the degenerate beam limiting the LOD to 2×10^{-5} absorbance units.

3 Molecular spectroscopy

The use of lasers in molecular spectrometry is widespread but concentrated in a few popular areas such as Raman spectrometry, LIDAR for remote sensing, and photothermal spectrometry. In addition there is a growing use of lasers as sampling devices in mass spectrometry particularly for the analysis of biomolecules, and proteins using the technique of matrix assisted laser desorption. Although strictly speaking MALDI is not a true spectrometric technique it is included in the review as a natural cousin to RIMS and LARIS as discussed earlier.

In addition to the major areas of Raman, LIDAR and photothermal spectrometry it should be noted that there are several diagnostic uses of laser spectroscopy, *e.g.* laser induced fluorescence, sub Doppler laser spectroscopy and optical–optical double resonance techniques, which provide extremely valuable information about individual molecular species. Few of these however can be exploited for routine analytical purposes and will not be considered further. A useful review of these techniques can be found in ref. 1.

Raman spectroscopy arises from the vibrational Raman effect due to the polarisability of molecular species. Application of an electric field gradient can induce a dipole of magnitude P, eqn. (3), where α is the polarisability of the molecule.

$$P = \alpha E \qquad (3)$$

If that electric field is induced by an electromagnetic wave; $P = \alpha E_o \cos(2\pi \nu_o t)$ where ν_o is the frequency of the wave and E_o is the amplitude of the electric field and the molecule is already vibrating at a frequency ν_{vib} its nuclear displacement from an equilibrium position q will be given by eqn. (4), where q_o is the vibrational amplitude. For a small amplitude of vibration α is a linear function of q. Thus it can be written as eqn. (5), where α_o is the polarisability at the equilibrium position.

$$q = q_o \cos(2\pi \nu_{vib} t) \qquad (4)$$

$$\alpha = \alpha_0 + \left(\frac{\delta\alpha}{\delta q}\right) q_0 \cos(2\pi \nu_{vib} t) \qquad (5)$$

Thus P can be written as eqn. (6).

$$P = \alpha_0\, E_0 \cos(2\pi \nu_0 t) + \frac{1}{2}\left(\frac{\delta\alpha}{\delta q}\right) q_0\, E_0 \{\cos(2\pi[\nu_0 + \nu_{vib}]t) + \cos(2\pi[\nu_0 - \nu_{vib}]t)\} \qquad (6)$$

Frequencies $\nu_o + \nu_{vib}$ and $\nu_o - \nu_{vib}$ appear in the spectrum as higher frequency and lower frequency lines with respect to the original polarising electromagnetic wave, *i.e.* the anti-Stokes and Stokes lines in the Raman spectrum. The Stokes lines are more intense than anti-Stokes lines because of the greater population of the ground state compared to the first excited vibrational level as predicted by the Boltzmann equation. The Stokes shift is typically of the order 100–3000 cm^{-1} and provides a degree of selectivity to Raman spectroscopy which has been utilised for a wide range of applications in both conventional dispersive mode Raman and latterly with Fourier transform raman spectroscopy.[21]

The Raman effect is weak and requires an intense light source such as a laser and extremely efficient collection optics with high stray light rejection to suppress the effects of laser line wings interfering with Raman shifted lines. Normally this requires a double monochromator or in recent instruments which employ CCD array detection, a combination of a notch filter and holographic grating to suppress the laser line and achieve adequate resolving power. Indeed this combination of instrumentation offers many exciting prospects for Raman process monitoring and Raman microscopy. Alternatively, high resolution Fourier transform instruments may be used to provide discrimination against the laser pump line although it is possible for noise on the Rayleigh line to be multiplexed into the Fourier spectrum if spectral filtering is inefficient and the instrument is source limited in terms of noise rather than detector limited.

In principle any laser could be used as it is the Raman shift which is of value not the absolute Rayleigh scattered line. In practice, however, near IR or visible region lasers are employed because Raman signals are not strong in the IR, principally because the Raman scattering efficiency is proportional to the fourth power of the laser line frequency. Also signal to noise ratios of photomultipliers in the UV–VIS region are much better than can be achieved with IR detectors.

Raman spectroscopy finds use in a very wide range of applications including inorganic and organic chemistry, polymer materials analysis, biological applications, process control and surface studies, the latter being particularly enabled through surface enhanced Raman processes. Raman has also been used for LIDAR studies as already mentioned for gases of environmental significance, *e.g.* CH_4, SO_2, NO_2. Other applications include catalyst studies and it is true to say that the technique is firmly embedded in industry as a versatile analysis tool. This versatility can only be enhanced by the replacement of large dispersive instruments by the current generation of notch filter based instruments with CCD detection which allows almost portable instruments to be configured with the ease of signal averaging and processing associated with array detectors. A good review of applications can be found in the work of Hendra *et al.*[21] for FT Raman spectrometry and the chapter by Averil in an Introduction to Laser Spectroscopy as cited in ref. 1.

Coherent anti-Stokes Raman spectroscopy (CARS) has similarities with degenerate four-wave mixing in that two beams are mixed coherently in a co-linear direction in the sample. Unlike DFWM however normally two laser frequencies are used, ν_1 and ν_2. The coherent mixing produces strong scattered light of frequency $2\nu_1 - \nu_2$ and if ν_2 is tuned to the resonance condition of $\nu_2 = \nu_1 - \nu_R$ where ν_R is a Raman active mode then $2\nu_1 - \nu_2 = 2\nu_1 - (\nu_1 - \nu_R) = \nu_1 + \nu_R$ is emitted coherently and over a small range of angles. The emitted beam can be detected without the use of a monochromator and any fluorescence is avoided appearing normally on the Stokes side of the pump line. In practice, the technique is employed for interrogating hostile environments such as combustion chambers, flue gases *etc.* An alternative is to use remote sensing techniques such as LIDAR.

4 LIDAR techniques

LIDAR is an acronym for light detection and ranging, a technique in which a powerful pulsed laser is used to probe remote hostile or inaccessible locations or atmospheres to deduce either chemical composition or aerosol and particle concentrations. The range of such measurements can be up to 10 km and in some cases ranges of 100 km are claimed.[22] LIDAR techniques can be broadly divided into three classes:

(*i*) scattering techniques (elastic or inelastic);
(*ii*) absorption and differential absorption techniques;
(*iii*) fluorescence techniques.

LIDAR techniques can be either single ended techniques where the laser source and receiver are at one location (*e.g.* scattering or fluorescence techniques) or double ended where either the detector is at a remote location on the beam propagation axis or a remote retro-reflector is used to return the beam. In the latter case it is often convenient to use a geographic feature or building as the reflector. Double ended techniques are usually employed to facilitate absorption measurements although the use of backscattering to discriminate between absorbed and non-absorbed radiation in the *differential absorption LIDAR* system (DIAL) permits single ended measurements to be made. Types of lasers used for LIDAR measurements are varied and depend upon the spectral region of interest. All are pulsed however to permit ranging by the use of gated detectors and with electronic boxcar averaging techniques. For non-spectroscopic measurements, *e.g.* Rayleigh or Mie scattering from aerosols, a single line laser may be used, for example a Nd:YAG in the near infra-red (1034 nm) which can be frequency doubled into the visible region using second harmonic generation techniques (532 nm). For spectroscopic measurements the use of Nd:YAG or excimer pumped dye lasers provides wavelength coverage over a spectral region between 400 and 800 nm. Again the range of such a laser system can be extended into the UV region using frequency doubling techniques.

A popular laser for LIDAR in the infra-red region is the CO_2 gas laser tunable over a large number of lines between 9.1 and 11 μm. Others include carbon monoxide lasers which have laser lines in the 5–7 μm region and hydrogen fluoride and deuterium fluoride lasers with lines in the 2.6–4 μm region. Thus it is possible to cover an extensive range of the UV, visible and IR regions of the spectrum albeit at discrete lines which must coincide with an absorption line in the atmosphere for absorption or fluorescence LIDAR to work. Semi-conductor lasers have found only limited application in LIDAR systems because the high powers required are not available with these devices. However a wide range of wavelengths are available in the visible and infra-red regions and they are tunable over a limited range and their use over short ranges could be beneficial.

There have been many applications of *Rayleigh and Mie scattering* LIDAR to the study of atmospheric aerosols and their role in climate modification. Typically, aerosol column densities are measured *via* elastic scattering measurements as well as aerosol shape and size parameters. Of particular interest is the role of aerosols on the climate and global energy balance. A recent study by Marshall *et al.*[23] has suggested that small differences in aerosol asymmetry parameter and hence scattering behaviour could cause significant changes in climate forcing *i.e.* imposed changes to the global energy balance. Stratospheric aerosol concentrations can be modified greatly by events such as the 1991 eruption of Mount Pinatubo which injected 12–20 megatons of SO_2[24,25] into the atmosphere which was subsequently converted in to 20–30 megatons of H_2SO_4. Vertical profiles of the particle mass and surface area concentrations in the stratospheric aerosol layer as a result of this eruption have been monitored by independently measured aerosol backscatter (particle and Rayleigh) and molecular backscatter (Raman and Rayleigh) measurements using a Raman LIDAR, showing persistence of the aerosol until at least Spring 1993. These measurements permit the retrieval of microphysical properties of the volcanic aerosol particles as well as pure molecular backscatter from atmospheric molecular species thus providing a powerful tool for atmospheric studies.

Rayleigh and Mie elastic scattering measurements are also routinely made in smokestack plume tracking for environmental purposes.[26] Combined with DIAL measurements for environmentally destructive pollutants such as SO_2, LIDAR offers the only plausible long-range tracking technique and its greater use is predicted even though there are significant operational problems as outlined below, and significant capital expenditure required.

Inelastic Raman scattering techniques have also been used for LIDAR measurements although sensitivity compared with say fluorescence and absorption techniques is poor because of the low Raman scattering cross section compared to absorption cross sections and the requirement for a high resolution spectrometer at the receiver end of the apparatus which inevitably results in very low light throughput even if detected at the receiving telescope. Thus a weak effect is compounded by stringent instrumental requirements. Nevertheless Raman LIDAR has been used because of the high spectral selectivity which can be obtained for simple Raman active gases of environmental importance, *e.g.* SO_2, N_2O, H_2S, CH_4. Again, for local stack monitoring on site where these simple pollutant molecules are present in reasonably high concentrations the Raman technique can be successfully applied.

5 Photothermal spectrometry

Photothermal spectrometry as a class of techniques comprises photoacoustic spectrometry, optothermal radiometry, photothermal beam deflection and thermal lens spectrometry. All rely upon the absorption of optical radiation by the sample. Subsequent non-radiative relaxation of excited chromophores results in local heating in the sample which can be detected and related to the absorption process taking place. Photoacoustic spectrometry is normally considered an ancillary technique to conventional spectrometry and is performed using a specialised cell in, for example, FTIR spectrometers. Detection of the generated thermal wave is achieved using a sensitive microphone in the PAS cell. There is a limited use of lasers in *laser induced photoacoustic spectrometry* (LIPAS) however, in which a modulated laser beam is used to generate a thermal wave in the sample which can be detected by measuring the sample surface displacement or by beam deflection methods in which a probe beam passes over the surface of the sample to probe the time dependent refractive index changes induced in the contacting medium. Depth profiling can be achieved by changing the modulation frequency of the laser beam which changes the thermal diffusion length in the sample. The technique has been successfully applied mostly to solid samples such as glass, semiconductors and skin to determine their optothermal properties. *Optothermal radiometry* has also been applied to these types of sample. In this technique a pulsed laser is used to irradiate a sample and the resulting thermal wave is detected as infra-red emission from the surface using a conventional IR detector. A recent review by Imhof[27] discusses the theoretical basis of the technique and areas of application.

For solution analysis perhaps the most popular and rapidly developing photothermal technique is *thermal lens spectrometry* (TLS) . In this technique the sample is illuminated with a TM_{oo} beam, *i.e.* of Gaussian radial intensity profile, focused into the sample. Absorption and subsequent non-radiative relaxation of chromophores results in a refractive index gradient which can be detected with a low power probe beam propagating co-linearly with the excitation beam. Because the temperature coefficient of refractive index is negative this gradient appears as a diverging lens to the probe beam hence the term 'thermal lens'. The relative divergence of the lens can be simply determined in the far field as a change in intensity using a pin-hole in front of a photodiode or as a change in beam profile using an array detector. Using a tunable dye laser it is feasible to obtain the absorption spectrum of compounds in solution although this can be a tedious procedure compared to say UV–VIS spectrophotometry owing to the limited spectral range of different dyes which necessitates frequent changing to cover the spectral range required. In practice therefore limited ranges are studied in the UV–VIS region. Nevertheless, thermal lens spectrometry has some convincing arguments for its use especially for trace analysis. It is much more sensitive being a power dependent technique as shown in the simplest form of the relationship between the thermal lens signal and power in which a parabolic approximation to the beam profile is assumed, eqn. (7), where P is the pump beam power, $\mathrm{d}n/\mathrm{d}T$ is the temperature coefficient of the refractive index, A is the absorbance of the solute or analyte and k is the thermal conductivity of the solvent.

$$S \alpha \frac{PA.\mathrm{d}n/\mathrm{d}T}{\lambda k} \tag{7}$$

Through the absorbance term S is proportional to the concentration of analyte. In addition to the power dependency enhancement of the signal can be achieved by appropriate choice of solvents with large values of $\mathrm{d}n/\mathrm{d}T$.

Typically detection limits are three to four orders of magnitude lower than obtained in UV–VIS, making it possible to analyse in the ppb range for many substances and metal ion complexes. Another advantage is that extremely small volumes of solution equivalent to the beam interaction volume (as little as 100 pl) can be interrogated leading to extremely small mass detection limits. There are many other applications of TLS in both the CW mode including capillary column detection, determination of absolute quantum efficiencies of dyes and determination of optothermal properties of solids, liquids and gases. In the pulsed mode using pulsed lasers many studies of excited state lifetimes, solute–solvent interaction, photochemical reactions and other time dependent processes have been reported which are too numerous to discuss here. The reader is referred to the review of Snook and Lowe[28] or the book of Bialkowski[29] for comprehensive reviews.

6 Laser mass spectrometry

The use of lasers in mass spectrometry is becoming widespread either as sampling and ionisation sources or for post source ionisation. Perhaps the most significant use is in *matrix assisted laser desorption/ionisation* (MALDI) in which a UV laser pulse is used to desorb and ionise or partially ionise analyte molecules from a UV absorbing substrate to produce MH^+ ions in the presence of MNa^+. This technique has found successful application for the analysis of biomolecules of high molecular mass and in particular for proteins up to a 500 kDa and detection limits of a few hundred femtomoles. Reviews on the subject abound but of particular note are those by Hillenkamp *et al.*[30] and Bahr *et al.*[31]

Commonly the source comprises a nitrogen laser (337 nm) or a frequency tripled or doubled Nd : YAG laser. Pulse durations are of the order of 1–200 ns with irradiances of 10^6–10^7 W cm^{-2} delivered through a laser spot size on the matrix in the range 50–500 μm. The analyte is isolated in a strongly UV absorbing matrix of low molecular mass molecules. The analyte must be incorporated in the crystalline matrix and this is achieved by mixing a dilute analyte solution with the matrix solution, transferring this to the mass spectrometer probe and allowing the solvent to evaporate. Selection of the matrix depends upon the solubility of the analyte and the laser wavelength available; typical matrices are 2,5-dihydroxybenzoic acid and synapinic acid for wavelengths in the region of 350 nm.

After absorption of laser radiation analyte is desorbed from the matrix and ionised as protonated ions. Although the exact mechanism of formation is not fully elucidated it appears to involve photoexcitation of the matrix followed by proton transfer to the analyte molecule. MALDI is normally used in conjunction with a *time-of-flight* (TOF) mass spectrometer because of the almost ideal short pulse of ions produced on desorption allows a complete mass spectrum to be obtained for each laser pulse. Although MALDI-TOFMS has found widespread use in the analysis of biopolymers such as proteins, oligosaccharides and oligonucleotides recent applications have also included synthetic polymers, indeed Mowat and Donovon[32] have applied MALDI to polystyrene and polybutadiene without a matrix simply by doping the sample with metal salts to facilitate cationisation under laser pulse conditions.

MALDI is not without problems, however, TOF spectrometers have in principle a very high mass limit (>300 kDa)—but the mass resolution is very poor (500 Da) and for this reason several applications of *Fourier transform ion cyclotron resonance* (FT-ICR) have been reported. With FT-ICR a lower mass range is accessible for singly charged ion (<20 kDa) but at much higher resolving power.

Further problems arise out of the variation of sensitivity between compounds for a given support matrix which can occur as well as variations due to irreproducible sample preparation. Nevertheless the future of MALDI is secure especially in bioanalytical and biological applications.

7 Summary

In the introduction the requirements for a successful analytical technique were outlined and it was implied that techniques such as ICP-AES, AAS, FTIR *etc.* have been successful in meeting these requirements. It is appropriate therefore that laser techniques be judged by the same criteria and if trying to achieve the same aims and performance of an existing technique that they should be judged against that technique. It is only when performance exceeds existing standards that laser-based techniques will be commonplace. It is difficult of course to define performance. For techniques such as LIDAR there is no credible alternative for remote stand-off detection which of course explains its adoption even though the technique is expensive and often difficult to operate. Other techniques will emerge however which will, in turn, be judged against the performance of LIDAR.

The atomic techniques described above can be compared to existing analytical techniques such as ICP-AES and ICP-MS and it is difficult to see how any of them will replace these giants of elemental analysis. Perhaps they should be seen as complimentary techniques. Certainly laser techniques have proved extremely valuable as diagnostic tools in plasma spectrometry as reported by Sesi *et al.*[33] Perhaps LEAFS has a chance based mainly on the extremely good detection limits obtainable but as already discussed there needs to be a debate on the meaning of such low concentrations of pollutants and perhaps the case cited concerned with the very pure environment of Greenland snow is relevant in this respect.

The case for degenerate four-wave mixing could also be made but from a diagnostic point of view. It is feasible to use the technique as a replacement for high resolution spectrometry as the technique provides a measurement of Doppler-free linewidths. Turning to laser induced breakdown spectrometry, there is some philosophical advantage to avoiding sample introduction and achieving direct solids analysis but the expense of fast digital acquisition and data handling besides the cost of the laser weighs heavily against the technique. Similarly, difficulties in calibration and unknown matrix effects holds up its acceptance as an analytical technique. On the other hand laser ablation as a sample introduction technique has a toe-hold but here it is used primarily in conjunction with an ICP so it is not really competing with traditional techniques, rather more complementing them.

Significant advances in laser techniques in analysis can be seen in molecular spectrometry, in Raman, LIDAR, and photothermal spectrometry. Raman is becoming increasingly a routine technique brought about by simplification of the instrumentation using notch filters and holographic gratings to provide smaller and more robust spectrometers to such an extent that they can now be employed for routine process control *via* optical fibre interfacing with the process plant. LIDAR as mentioned has no real competitors for stand-off chemical analysis, especially at greater distances (>10 km) and its wide use in meteorological, atmospheric and environmental pollution monitoring is predicted.

In the photothermal techniques some useful ways of interrogating extremely small sample volumes can be achieved to provide essentially the same information as UV spectrometry but at greater sensitivity. Nevertheless there is still the cost constraint involved in accessing the blue end of the visible spectrum and the UV region. So long as excimer lasers, frequency doubled dye lasers or OPOs are required then the cost of accessing this important region of the spectrum will be high and prohibit the widescale use of lasers to replace conventional techniques even if performance figures are better. Clearly the way ahead is the development of cheaper, more blue diode laser devices which are tunable over a wide wavelength range in the UV–VIS region. Until this happens laser spectrometry will be confined to the red, the near infra-red and infra-red regions of the spectrum in the specific areas described in this review. Like every other analytical laser spectrometrist I await keenly further developments at the blue end of laser technology!

8 Glossary of acronyms

AAS	Atomic absorption spectrometry
BBO	β phase barium borate
CARS	coherent anti-Stokes Raman spectrometry
CCD	charge coupled device
CW	continuous wave
DFWM	degenerate four-wave mixing
DIAL	differential absorption Lidar
FT-ICR	Fourier transform ion cyclotron resonance
FTIR	Fourier transform infra-red

ICP-AES	inductively coupled plasma atomic emission spectrometry
ICP-MS	inductively coupled plasma atomic mass spectrometry
LA-ICP-AES	laser ablation inductively coupled plasma atomic emission spectrometry
LARIS	laser ablation resonant ionisation spectrometry
LEAFS	laser enhanced atomic fluorescence spectrometry
LIBS	laser induced breakdown spectrometry
LIDAR	light detection and ranging
LIPAS	laser induced photoacoustic spectrometry
MALDI-MS	matrix assisted laser desorption mass spectrometry
Nd^{3+}YAG	Neodymium yttrium aluminium garnet
OPO	optical parametric oscillator
RIMS	resonance ionisation mass spectrometry
SIMS	secondary ion mass spectrometry
TLS	thermal lens spectrometry
TOFMS	time of flight mass spectrometry
TRELIBS	time resolved LIBS

9 References

1 M. R. S. McCoustra, in *An Introduction to Laser Spectroscopy*, ed. D. L. Andrews and A. A. Demidov, Plenum Press, New York, 1995.

2 J. Hecht, *The Laser Guidebook*, 2nd Edn. McGraw Hill, New York, 1992.

3 J. Pfab, *Laser Induced Fluorescence Spectrometry* in *Applied Laser Spectroscopy: Techniques, Instrumentation and Applications*, ed. D. L. Andrews, VCH Publishers Inc., New York, 1992.

4 D. J. Butcher, F. R. Dougherty, A. P. Preli Walton, W. Guour-Tzo, R. L. Irwin and R. G. Michel, *J. Anal. Atom. Spectrom.*, 1988, **3**, 1059.

5 E. P. Wagner, B. W. Smith and J. D. Winefordner, *Anal. Chem.*, 1966, **68**, 3199.

6 M. A. Bolshov, V. G. Koloshnikov, S. N. Rudnev, C. F. Boutron, U. Gorlach and C. C. Patterson, *J. Anal. Atom. Spectrom.*, 1992, **7**, 99.

7 J. C. Travis and G.C. Turk, *Laser Enhanced Ionisation Spectrometry*, vol. 136 *Monographs in Chemical Analysis.*, ed. J. D. Winefordner, Wiley Interscience, New York, 1996.

8 N. Omenetto, B. W. Smith, P. B. Farnsworth and J. D. Winefordner, *J. Anal. Atom. Spectrom.*, 1996, **7**, 89.

9 G. G. Hurst and M. G. Payne, *Principles and Application of Resonance Ionisation Mass Spectrometry*, Adam Hilger, Bristol and Philadelphia, 1988.

10 K. W. D. Ledingham, *Multiphoton Ionisation and Laser Mass Spectrometry* in *An Introduction to Laser Spectroscopy*, ed. D. L. Andrews and A. A. Demidov, Plenum Press, New York, 1995.

11 H. F. Arlinghams, N. Thonnard, M. T. Sparr, R. A. Sachleben, G. M. Brown, R. S. Foote, F. V. Sloop, J. R. Petersen, and K. B. Jacobsen, *J. Vac. Sci. Technol.*, 1991, **A9**: 1312.

12 D. A. Cremers, L. J. Radziemski and T. R. Loree,, *Appl. Spectrosc.*, 1984, **38**, 271.

13 L. J. Radziemski, T. J. Loree, D. A. Cremers and N. M. Hoffman,, *Anal. Chem.*, 1983, **55**, 1246.

14 R. W. Wisbrun, R. Niessner and H. Schroeder, *Analytical Methods and Instrumentation*, 1993, **1**, 17.

15 R. W. Wisbrun, I. Schechter, R. Neissner and H. Schroeder, *Proc. SPIE*, 1993, 1716.

16 M. Casini, M. A. Harith, V. Palleschi, A. Salvetti, D. P. Snigh and M. Vaselli, *Laser and Particle Beams*, 1991, **9**, 633.

17 K. Dittrich, and R. Wennich,, ch. 5, in *Sample Introduction in Atomic Spectroscopy*, ed. J. Seddon, Elsevier, New York, 1990.

18 H. Groll, Ch. Schruerer-Patschan. Yu. Kutitsyn and K. Niemax, *Spectrochim. Acta B*, 1995, **49**, 1463.

19 J. M. Ramsey, and W. B. Whitten, *Anal. Chem.*, 1987, **59**, 167.

20 T. de Beer, G. Ph. Hoornweg, G. J. Grootendorst, N. H. Velthorst and C. Gooijer, *Anal. Chim. Acta*, 1996, **330**, 189.

21 P. Hendra, C. Jones and G. Warnes, *Fourier Transform Raman Spectroscopy*, Ellis Horwood Ltd., Chichester 1991.

22 C. B. Carlisle, J. E. van der Laan, L. W. Carr, P. Adam and J. P. Chiaroni, *Appl. Opt.*, 1995, **34**, 6306.

23 S. F. Marshall, D. S. Covert and R. J. Charleson, *Appl. Opt.*, 1995, **34**, 6187.

24 G. J. S. Bluth, S. D. Doiron, A. J. Krueger, L. S. Walter and C. C. Schnetzler, *Geophys. Res. Lett.*, 1992, **19**, 151.

25 R. D. Peters, *Geophys. Res. Lett.*, 1993, **20**, 1971.

26 S. Sutton and M. Bennett, *Int. J. Remot. Sens.*, 1994, **15**, 375.

27 R. E. Imhof, A. D. McKendrick and P. Xiao, *Rev. Sci. Inst.*, 1995, **66**, 5203.

28 R. D. Lowe and R. D. Snook, *Analyst*, 1995, **120**, 2051.

29 S. E. Bialkowski, *Photothermal Methods for Chemical Analysis*, vol. 134, Chemical Analysis–Monographs, Wiley Interscience, 1996.

30 F. Hillenkamp, M. Karas, R. C. Beavis and B. T. Chait, *Anal. Chem.*, 1991, **63**, 1193A.

31 U. Bahr, M. Karas and F. Hillenkamp, *J. Anal. Chem.*, 1994, **348**, 783.

32 I. A. Mowat and R. J. Donovon, *Rapid Commun. Mass Spectrom.*, 1995, **9**, 82.

33 N. N. Sesi, D. S. Hauselman, P. Galley, J. Horner, M. Huang and G. M. Hieftje, *Spectrochim. Acta B*, 1997, **52**, 83.

Received, 14th February 1997
Accepted, 23rd April 1997