Development of double-pulse lasers ablation system and electron paramagnetic resonance spectroscopy for direct spectral analysis of manganese doped PVA polymer

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Abstract
Series of manganese-co-precipitated poly (vinyl alcohol) (PVA) polymer were quantitatively and qualitatively analyzed using laser ablation system (LAS) based on double-pulse laser induced breakdown spectroscopy (DP-LIBS) and electron paramagnetic resonance (EPR) spectroscopy. The collinear nanosecond laser beams of 266 and 1064 nm were optimized to focus on the surface of the PVA polymer target. Both laser beams were employed to estimate the natural properties of the excited Mn-PVA plasma, such as electron number density (N_e), electron temperature (T_e), and Mn concentration. Individual transition lines of manganese (Mn), carbon (C), lithium (Li), hydrogen (H) and oxygen (O) atoms are identified based on the NIST spectral database. The results show better responses with DP-LIBS than the single-pulse laser induced breakdown spectroscopy (SP-LIBS). On the other hand, the EPR investigation shows characteristic broad peak of Mn-nano-particles (Mn-NPs) in the range of quantum dots of superparamagnetic materials. The line width (peak-to-peak, ΔH_{pp}) and g-value of the observed Mn-EPR peak are ~20 mT and 2.0046, respectively. The intensities of Mn-emission line at a wavelength 403.07 nm and the Mn-EPR absorption peak were used to accurately quantify the Mn-content in the polymer matrix. The results produce linear trends within the studied concentration range with regression coefficient (R^2) value of 0.99, and limit of detection (LOD) of 0.026 mol.% and 0.016 mol.%, respectively. The LOD values are at a fold change of about ~0.2 of the studied lowest mol.%. The proposed protocols of trace element detection are of significant advantage and can be applied to the other metal analysis.

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1. Introduction

Poly-vinyl alcohol, PVA, polymer matrix has excellent biocompatibility, bio-degradability, and of lightweight material. It is widely used in pharmaceutical, biomedical applications such as drug delivery systems, artificial pancreas and skin and cardiovascular device [1,2]. The metal additives were embedded in a pure PVA polymer to be utilized as a solid polymer electrolyte in electrochromic displays [3].

The water-soluble synthetic polymer is one of the great advantages of PVA films. The addition of manganese in the PVA polymer could make the structure of high mechanical strength, more stable. Detection of trace additives are needed to establish a feasible recycling process for speedy automated sorting systems.

The inductively coupled plasma–mass spectrometry (ICP-MS) and Raman spectroscopy (RS) techniques were utilized, which can obtain a lower limit of detection (LOD). But both techniques are time-consuming, expensive and required iterative target preparation with digestion of concentrated acids to dissolve hard samples. Moreover, some elements like carbon (C) and manganese (Mn) are rough to be detected with such conventional techniques.

Laser wavelength, distance from the target surface, angle of observation and lasers pulse energy ratio are of great importance in setting up the experimental conditions for optimum plasma performance. The detection of heavy elements in polymers with LIB spectroscopy has been studied by several researchers [4–6]. For example, a single-pulse LIBS was used for the detection of halogen atoms (Cl and Br) in thermoplastic and flame retardant polymers [7–9] and heavy metals in plastics [10,11]. Similarly, poly (vinyl chloride), PVC, has been studied by Sattmann et al. [12] for the chlorine (Cl) line. Therefore, it was concluded that the...
experimental environments for the polymer LIBS analysis under air or vacuum still need more optimization and development [13]. On the other hand, the electron paramagnetic resonance (EPR) spectroscopy was successfully employed as an analytical technique to monitor the existence of several paramagnetic species in natural or synthetic materials. The EPR also used to investigate the thermal endurance of the PVC and XLPE power cable insulation polymer materials [14]. The results estimated more accurately the lifetime of these polymer materials compared to the known standard methods [15]. It has also confirmed the fact that PVC is rapidly degraded than XLPE.

Recently, a spectral analysis of metal nanoparticles in glass materials (host material) using DP-LIBS and EPR spectroscopic techniques have been a subject of interest due to their new behavior [16]. The work indicated that the ionization and excitation processes following breakdown are important for understanding the mechanism of laser radiation on any target.

In this work, both EPR and DP-LIBS techniques for analyzing nano-metal-polymer materials are studied. Those methods are non-destructive and require “minimal” target preparation. It is the first work on the use of EPR and/or DP-LIB spectroscopic techniques for the measurement of a Mn content in PVA polymer, to the best of our knowledge. The results depicted the correlation between the EPR and DP-LIBS techniques of Mn-analysis in the PVA polymer matrix. Both methods show a very low limit of Mn-detection (LOD) compared to others typical methods. The work provided advice for the choice of the experimental conditions and parameters for material testing applications.

2. Experimental procedures

2.1. Materials and polymer preparation

PVA was purchased from Sigma–Aldrich (MW = 124,000–186,000, 90.99% degree of hydrolysis). Manganese reference standard solution (1000 ppm ± 1%) was purchased from Fisher Chemical for EPR calibration. MnSO₄ from Sigma–Aldrich with 99.2% purity for doping the polymer by mixing proper concentrations of 0.1, 0.3, 0.6, and 0.9 mol.% of manganese into aqueous solutions of PVA (C₅H₁₂O₂, MF = 104.15) matrix. These mixtures have been utilized to prepare a series of 4 mm thick polymer samples that are cast on a glass plate. The samples were dried in evacuating desiccator. The thickness of each sample was determined by using a micrometer of ±0.01 mm accuracy.

2.2. Double-pulse LIBS geometry

The layout of the collinear DP-LIBS geometry setup for the analysis of the Mn-PVA matrices is shown in Fig. 1 part A. Briefly experimental details of our DP-LIBS emission spectroscopy can be found elsewhere [17]. The lasers arrangement includes a 266 nm lasers I (Continuum model NY81-30) of 7 ns pulse duration and 30 Hz repetition rate used for ablation process and a 1064 nm laser II (Spectra Physics INDI-50) of 6 ns pulse width and 30 Hz repetition rate utilized for the second pulse. The collinear DP-geometry of the lasers beams operating at 266 and 1064 nm wavelengths and 25 and 300 mJ laser energies, respectively, are used to generate the plasma at different separation from the surface of the Mn–PVA target (Fig. 1 part B). The energies of both lasers are optimized continuously with a 3-Sigma energy meter, Coherent, USA, by adjusting the voltage of the flash lamps.

Various pairs of harmonic nanosecond lasers were studied to achieve better optimization. Hence, it is confirmed that the integration of 266 + 1064 nm gives the maximal S/N ratio where a fundamental IR laser (II) is triggered by a UV laser (I) signal. The intensity distribution within each laser beam was in Gaussian profile, i.e. TEM₀₀ mode, which is described by the Gaussian fitting function of a correlation Ρ = 0.90 with an M² ρ = 1.53 and shot-to-shot stability ρ = 7%. The combined laser beams were focused on the sample using a lens (focal length, f = 50 cm). The focusing was tested at a different separation from the specimen surface (Fig. 1 part B) and an Airy disk spot size by diameter of first zero rings of the laser beam, which is defined as

\[ d_0 = 2.44 \lambda / D \]

where \( \lambda \) is the wavelength and \( D \) is input beam diameter. The focal spot diameter at the focus was obtained on exposed Polaroid film in the range of 350–400 μm, which yields an area of \( 10^{-3} \text{ cm}^2 \). The testing DP-laser beams focused distances from the polymer surface are as follows: \( d = -2.5 \text{ mm}, -1 \text{ mm in front of the surface}; d = 0, \text{ at the surface}; d = 3 \text{ mm, 4 mm behind the surface}. The inter-pulse delay \( \Delta t \) between the pair of laser pulses has also been ranged from 0 to 500 ns to enhance the S/N ratio that was measured with a photodiode and fast oscilloscope and was adjusted by using a Stanford delay generator DG535 of 1 ns timing jitter.

The laser determination of manganese was conducted with Mn-PVA polymer sample in the form of a disc having 4 mm thickness and 50 mm diameter that is rotated with a rotary disc of adequate speed using a motorized X-Y translation holder stage to provide a new surface. The translation holder stage was controlled by software to suppress the development of any crust and obtain a new surface for every burst of laser shots. The plasma generated by the laser beam induced light emission that is collected by a fixed lens on the slit of a high-resolution spectrometer (0.5 nm, SPEX) with Multimode fiber lens of 0–45° field of view. The spectrum was recorded in the domain of 300–950 nm with 0.5 nm resolution. Synchronization between the gated camera (intensiﬁed charge coupled device (ICCD), Princeton Instrument) and the laser pulse has been obtained. The average of ten scans has been accumulated to conquer the statistical fluctuations that are also used.
to estimate the relative-standard-deviation (RSD) of the observed maximum intensity.

2.3. EPR spectroscopy system

An upgraded EPR spectrometer (MS300 MiniScope, GmbH Magnet-tech, Germany) with a CMS8400’s ADANI worked at the X-band was employed at room temperature to obtain the EPR spectra of PVA samples. All measurements were achieved using a TE102 cavity with rectangular shape operated at 9.4 GHz microwave bridge. A rectangular polymer film dimensions of samples 0.1 (T) × 4 (W) × 10 (L) mm² were hosted in an EPR tissue cell of a flat part (target holder; dimensions 65 × 7 × 2 mm³) and a cover slide. A PVA film with and without Mn-doping was carefully sandwiched between the two EPR quartz tissue plates. The EPR spectrometer working with microwave of frequency = 9.42 GHz, sweep time = 60 s, signal gain = 20, attenuation = 12 dB, modulation amplitude = 100 μT, and target temperature ~28 °C. These contributing parameters were selected to enhance the recorded signal intensity. Then, the EPR spectra of the PVA and its Mn-doped samples were observed as first derivative spectra at the largest values of the magnetic flux.

3. Results and discussion

3.1. DP-LIB spectroscopic determination of Mn-PVA polymer

At 40 μs gate width, 100 μm slit width, and 1.25 × 10¹⁹ W/cm² laser irradiance, the optimum experimental condition of DP-LIB, the recorded spectra are presented in Fig. 2(A–C). The ranges 239–480, 480–600 and 600–800 nm of the scan are used to cover UV–Vis regions and to elucidate the emission lines of major elements in the Mn-PVA polymer matrix. Individual transition lines of manganese (Mn), carbon (C), lithium (Li), hydrogen (H) and oxygen (O) atoms are identified based on the NIST spectral database [18]. A summary of these transitions are listed in Tables 1 and 2. Some of the lines show a broadening on the continuum of dual pulse LIB spectra that could be attributed to the electronic elastic collisions with ions. The delay between the laser trigger signal pulse LIB spectra that could be attributed to the electronic elastic maxima at 0.5 l mm, from the surface of the Mn-PVA specimen. A gradual

3.2. Plasma parameter measurements

The Boltzmann plot and Stark broadening employed, in this study, to estimate the electron temperature, Te and density, Ne, respectively, as the population of the excited upper levels obeys a Boltzmann distribution with an emissivity (ε_Ak) as [22],

\[ \ln \left( \frac{A_k \varepsilon_k}{\Lambda_k \varepsilon_0} \right) = \frac{-E_i}{kT_e} + \ln \left( \frac{M(T)}{U(T)} \right) \]

where \( A_k \) is the transition probability; \( g_i \) is the statistical weight and \( A_k \) is the wavelength. The \( E_i \) is the energy of upper state; \( k \) is the Boltzmann constant; \( U (T) \) is the partition function, and \( M(T) \) is the ion density. The \( T_e \) values were calculated of the PVA-Mn doped polymer plasma for all the observed spectral lines, namely, Mn-280.11 nm, Mn-355.97 nm, Mn-284.03 nm, Mn-369.65 nm, and Mn-403.07 nm. A plot of \( \ln \left( \frac{A_k}{\Lambda_k} \right) \) versus the energies of upper level (\( E_i \)) gives a straight line with a slope (−1/KT) for single pulse (SP) and DP geometry as shown in Fig. 6A, that the \( T_e \) s can be estimated from the obtained slope. This plot was used to explain the dependence of the \( T_e \) s along the plasma plume on the separation from the Mn-PVA surface for the plasma generated by the 266 nm SP laser, 1064 nm SP laser, and (266 + 1064 nm) DP-lasers geometries as depicted in Fig. 6B. The results showed that the \( T_e \) varies from 4030 to 823 K in the distance (0–1.5 mm) region for the Mn-PVA excited plasma by 266 nm SP-laser, and from 9210 to 4100 K in the distance (0–2 mm) domain by 1064 nm SP-laser. While \( T_e \) varied from 12,300 to 7000 K in the distance (0–2.75 mm) region for the Mn-PVA excited plasma by the DP-laser pulses operating at (266 + 1064) nm. It can be noted that the \( T_e \) is hotter in DP-LIB by nearly 3 times as compared to SP-LIB spectrum. The \( T_e \)’s are hotter near the Mn-PVA surface and reduce along the plume expansion, axis in the both (SP and DP) cases. In SP geometry, the value of \( T_e \)’s reduced fast while in the case of DP geometry, it reduces slowly (approximately linear). The error bars indicated to the standard deviation...
of ten repetitions of observation amassed during the recording of each spectrum.

The $N_e$ is predicted by using the following equation,

$$D_{k_{1/2}} = 2A \left( \frac{N_e}{10^{16}} \right) + 3.5A \left( \frac{N_e}{10^{16}} \right)^{1/4} \times \left[ 1 - \frac{3}{4} N_B^{1/3} \right] \omega \left( \frac{N_e}{10^{16}} \right)^{1/2} \lambda_{k_{1/2}}$$

(3)

where $\Delta \lambda_{k_{1/2}}$ is the spectral line width. $A$ and $\omega$ are the ion and electron-impact broadening parameters. $N_B$ is the particles number in the Debye sphere. The 1st term in this equation is the electron-impact broadening contribution, and it is weakly dependent on temperature [23] to make the line-width related to the 1st term and give

$$\Delta \lambda_{k_{1/2}}(A) = 2A \left( \frac{N_e}{10^{16}} \right)$$

(4)

where the actual line width $\Delta \lambda_{k_{1/2}}$ of Mn-403.07 spectral line is estimated by eliminating the instrument line width from the observed line as,
The predicted line width of the dual-pulse LIB spectrometer is 0.06 nm. The corresponding error is sacrificial 9%, and the width of the Mn-403.07 line is closed by a Lorentzian profile as shown in Fig. 7A. This figure depicts the DP-LIB signal intensity of the emission line Mn-403.07 nm to measure \( D^k_{1/2} \). The relative value of \( x \) (Stark width parameter) is \( 5.91 \times 10^{-3} \) nm and substituting the value of \( D^k_{1/2} \) could be used to determine the Ne value. Also, the local thermodynamic equilibrium (LTE) conditions are checked for the selected Mn-403.07 nm transition of the Mn-PVA target [25]. In our case the transition of the Mn-403.07 nm is \( 3d^5 4s^2 \) (6S) to \( 4s 4p \) (3Po) and the \( N_e \) lower limit value is \( 0.5 \times 10^{14} \) cm\(^{-3}\).

Similarly, in Fig. 7b the, electron number density close to the target surface in 1064 or 266 nm single pulse lasers and combined norm at all distances from the Mn-PVA target [25]. In our case the transition of the Mn-403.07 nm is \( 3d^5 4s^2 \) (6S) to \( 4s 4p \) (3Po) and the \( N_e \) lower limit value is \( 0.5 \times 10^{14} \) cm\(^{-3}\).
(266 nm) lasers are 1.23 × 10^{15} \text{ cm}^{-3}, 3.24 × 10^{15} \text{ cm}^{-3} and 7.51 × 10^{15} \text{ cm}^{-3}, and then decreases non-linearly to 1.51 × 10^{14} \text{ cm}^{-3}, 2.75 × 10^{14} \text{ cm}^{-3} and 9.88 × 10^{14} \text{ cm}^{-3} starting from 0.3 mm from the PVA surface, respectively. In the case of DP lasers, it was observed that the Ne has a peak up to 0.4 mm and then decreases up to 3 mm.

The inverse Bremsstrahlung process (IBP) is represented by the inverse-absorption-length ($\Phi_{ib}$) as a function of the wavelength of the laser $\lambda$ (\text{m}), which is presented as [26]:

$$\Phi_{ib} (\text{cm}^{-1}) \approx 1.37 \times 10^{-35} \lambda^4 N_e T_e^{-1/2}$$

The $\Phi_{ib}$ is about 0.3 cm$^{-1}$ at the laser intensity of $6 \times 10^{10}$ W/cm$^2$ that implies $1.7 \times 10^8$ W/cm$^2$ is absorbed in the plasma, which is nearly five folds higher than 266 nm SP laser. It can be seen from Fig. 6b that the $T_e$ is hotter for 1064 nm SP than 266 nm SP laser. That means the IBP is more efficient for IR as compared to UV SP lasers since of its $\lambda^4$ dependence (Fig. 5b). While in Fig. 7b, the various values of $N_e$ for the IR and UV as SP lasers depends upon the coupling of the laser beam with the PVA surface. Just the plasma is generated; its growth governed by the photo-ionization (PI) process of the excited atoms. In our Mn-PVA target, the ionization potential of the excited states is higher for 266 nm UV photons (3.23 eV) than at 1064 nm (1.02 eV). Therefore, the $N_e$ for 266 nm is greater than that of 1064 nm laser. Also, the highest value of $N_e$ for 266 nm rather than 1064 nm, is due to the mass ablation is greater for UV and has a lower value for the IR laser. Consequently, the mass ablation is higher for the combination of DP lasers than that obtained with SP-laser as shown in Fig. 7b. The measured density (7.51 × 10^{15} \text{ cm}^{-3}) in DP-LIB is larger than the value of the polymer plasma. Also, the LPE has been optimized until the laser saturates at a certain value of the pulse energy as follows: 25 mJ/pulse for SP at 266 nm, 50 mJ/pulse for SP at 1064 nm and 63 mJ/pulse for DP at (266 + 1064) nm. Certain values are observed from the employing of McWhirter criterion to the various recording conditions. Above the certain value of LPE, the
free negative charge species in the hot plasma absorb more laser photons, and the inverse Bremsstrahlung (IB) influences are considered.

We checked many pairs out of 1064 nm and harmonics of Nd:YAG lasers of the DP-LA system under the same optimization condition and confirmed that the combination 266–1064 nm revealed to enhance the signal-to-noise ratio (SNR) in comparison with the SP measurements, i.e. \( \text{SNR}_{\text{DP}} / \text{SNR}_{\text{SP}} \). The transition maximum after removing the background spectrum is called signal while the standard deviation of the corresponding background is called noise. A set of gauges was extensively optimized to advance the sensitivity of the UV–NIR spectra and to prolong the plasma life time. The 266 nm laser (shorter wavelength) as first pulse is more efficient in achieving ionization, bond breaking processes, non-thermal higher ablation rates, allowing for the formation of a controlled plasma, and coupling to the Mn-PVA target because of reduced shielding effects resulting in increased mass ablation as compared to 1064 nm pulses. The use of 266 nm laser for LAS also has shorter optical penetration depth, which offers greater laser energy per unit volume for ablation. Hence, the 1064 nm laser (longer wavelength) as second pulse provides controllable energy addition through the mechanism of inverse bremsstrahlung absorption with a lower ablation rate and interacts with rarefied ambient conditions, which further ablates the target as well as excites or re-heats the plasma plume produced by 266 nm laser pulse [27–30]. Thus, it is better to employ a sequence of short (266 nm) and long (1064 nm) wavelength lasers for DP-LAS as pre-ionization and reheating beams. In addition, higher temperature and electron density were recorded due to multi-photon ionization (MPI) driven nature of LAS plasma created by 266 nm laser pulse followed by re-heating and/or further ablation by 1064 nm pulse.

The \( T_e \) and \( N_e \) tendencies registered in this work are matched with the tendencies obtained in other concluded work [31]. Both \( T_e \) and \( N_e \) have been estimated at fixed 0.9 mol.% Mn concentration and \( d = 2 \) mm behind the polymer surface. The increase in the \( T_e \) and \( N_e \) with the increase of Mn mo.l.% concentration may be revealed to the fluorescence enhancement and extra collisions between the plasma charges. Fig. 8 depicts the vast variety of the line width of Mn-403.07 nm with the change of Mn concentrations in the range from 0.01 to 0.9 mol.%. The Mn I 403.07 nm line widths measured as a function of the manganese concentration in the Mn-PVA sample.

The Te and Ne tendencies registered in this work are matched with the tendencies obtained in other concluded work [31]. Both \( T_e \) and \( N_e \) have been estimated at fixed 0.9 mol.% Mn concentration and \( d = 2 \) mm behind the polymer surface. The increase in the \( T_e \) and \( N_e \) with the increase of Mn mo.l.% concentration may be revealed to the fluorescence enhancement and extra collisions between the plasma charges. Fig. 8 depicts the vast variety of the line width of Mn-403.07 nm with the change of Mn concentrations in the range from 0.01 to 0.9 mol.%. The Mn I 403.07 nm line widths measured as a function of the manganese concentration in the Mn-PVA sample.

3.3. SP and DP-pulses signal intensity dependence of the Mn ions angular distribution

We developed a special holder attached with an optical fiber for detecting the plasma emission at various angles (20–80°) as depicted in Fig. 9. The main important point on this work is to study the dependence of SP and DP signal intensities on the angle of detection in order to decrease measurement uncertainty and enhance light gathering efficiency. It can be see that the intensity of Mn at 403.07 nm increases with the increasing of collection angle with a maximum at 80° for SP (266 nm), SP (1064 nm) and DP (266 + 1064 nm). The LIBS signal intensity of the Mn (403.07 nm) spectral line is higher by factor of about 2 for DP experiment than that obtained by SP experiment. The highest intensity was reached at an angle of 80° in both SP and DP configurations. The inset in Fig. 9 depicts the plasma images produced by single and double laser pulses using accumulation side spectra. It is worth noticing here that the plasma is much extends and further larger above the Mn surface in the case of double pulse excitation compared to the single pulse excitation. In addition, the plasma plume seems to form a spherical shape with a little hot spot in the center near the target surface.

3.4. EPR spectra measurements and analysis

The electron paramagnetic resonance (EPR) became one of the most sensitive and adequate methods for investigating the...
structure and properties of different paramagnetic molecular systems, in which the unpaired electron retained its paramagnetic properties. It has been used for the direct determination of metals that have unpaired electrons in a stable oxidation state: Cu(II), Cr(III), Fe(III), Mn(II), and V(IV) [32–34]. Several applications of quantitative EPR have been [31–37] reviewed, including assays for vanadium [37], iron, manganese [38], and even for diamagnetic metals chelated to spin-labeled ligands [39]. Two reviews on quantitative EPR and quality control in EPR that are a bit hard to find are appended [38,39]. These works indicated that the EPR is a more selective than many conventional analytical systems and its strength come from its any samples, including whose scattering properties or opacity preventing the quantitative optical techniques. Fig. 10 shows a broad EPR spectrum of a PVA polymer film sample containing 0.9 mol.% Mn (II) placed between the quartz plated of the EPR-tissue sample holder. The observed peak is entirely overlapped with a well-resolved sextet spectrum of a 1000 ppm Mn (II) standard aqueous solution filled into a 3 mm (OD) multi-bore capillary tube, each of 0.5 mm (ID). Both spectra are positioned around 335 mT and are extended over ~200 mT. The values of the magnetic field at resonance (H) and resonance line width (ΔHpp) are 336.1 mT and 20 mT, respectively. The g-value is proportionality constant between the field and the frequency. It is a function of both the motion of the molecules and the symmetry of ions. The value of g is determined for the observed line as a function of the microwave frequency (ν), the Bohr...
magneton ($\beta$) and the resonance magnetic field ($H$) by the following equation:

$$g = \frac{hv}{\beta H}$$  \hspace{1cm} (7)

where $h$ is a Planck constant. The exact value of $g$-factors or both lines is found to be $\sim 2.0046$.

The featureless/strong, broad signal on the Mn-PVA polymer is an unresolved broad EPR line of a powder metal paramagnetic species [40]. It is also so similar to those of a well-bounded Mn (II) to protein system, namely ATPase, ADP, or ANP-BNP that shows more broadening upon bound to macromolecules [41,42]. Mn (II)-EPR broad signal is also depicted at Mn-nano-particles in superparamagnetic materials [43]. On the other hand, the completely unbounded Mn (II)-ions in the standard solution produced a well-resolved sextet of Mn (II) with $3d^5(6S^5/2)$ configuration, which exists in its high spin state ($S = 5/2$) [44–46]. Both spectra are fitted to the standard Hamiltonian of Mn (II)-system. Thus, the broad peak of Mn-PVA could be the net of the sextet peaks of either Mn (II)-bounded to the polymer or Mn (II)-oxide nanoparticles. In some protein, the broad peak of Mn (II) superimposed a weak sextet feature that is a characteristic of a partially unbounded Mn (II) elements to proteins [47–49]. The partially unbounded Mn is not observed in the Mn-PVA system that suggests the manganese in the polymer matrix is not the same form of protein. The observed brownish colored polymer suggested the Mn in PVA should be in the shape of nano-particles. This result is in good agreement with Zipare et al. results [50] of a nano-particle within a quantum dots’ particle size, i.e. in the range of 2–5 nm.

3.5. Quantitative and qualitative analysis of manganese in PVA

The quantification and calibration curve of the manganese element in the PVA have been analyzed based on both the DP-LIBS marker lines of Mn-403.07 and the EPR spectral lines using controlled samples with known concentrations. In Fig. 11(A–C), a picture of PVA targets of different manganese loadings from 0.1 to 0.9 mol.% employed in DP-LIBS experiment and their Mn-403.07 nm spectral line results. The instrumental auto-integrator was applied to determine the noise level, and hence the plotting of their DP-LIBS signal intensity is presented in Fig. 11 part C versus the initial Mn-ion concentrations. The linear fit represents the trend of DP-LIBS-Mn-403.07 intensity versus Mn concentration following the linear fitting equation $I_{DP} = a + bc$. The $I_{DP}$ is the DP-LIBS intensity; $C$ is the concentration; and $a$ and $b$ are the intercept and slope of the fit, respectively. Within the selected concentration range, the observed linear calibration curve has high values of the correlation coefficient ($R^2 = 0.987$).

The optimum inter-pulse delay, gate width, LPE, repetition rate, pulse duration, laser wavelength and laser focus position relative to the PVA surface sample have been used to get the most precise experimental data. These including the maximum S/N ratio that is obtained at the inter-pulse delay, $\Delta t$, equal to 250 ns, the time between the 1st excitation laser signal and the recording gate signal with a gate-delay, $t_g$, equal to 0.3 $\mu$s. Also, ten laser signals were averaged to reduce the relative standard deviation (RSD) of the DP-LIBS results that relates to the analytical instrument precision and was given as [51]:

$$\text{RSD} (\%) = \left(\frac{\text{Standard deviation (SD)}}{\text{mean}}\right) \times 100 \hspace{1cm} (8)$$

The precision of our results rely on the reproducibility of laser signals and the homogeneity of the Mn-PVA polymer sample. The typical procedure was applied to other spectral lines where we found that the precision varied between 3% and 5%, for example, RSDs were 3.5% for Mn, 3.7% for C, 1.5% of H, 4% for Li, 1.2% for O.

In the case of the EPR measurements of Mn-doped PVA samples, we used a Lorentzian distribution function to analyze the results and determine the values of some parameters. Many EPR scans per specimen were acquired, and their peak-to-peak intensities were obtained to determine the manganese content in several PVA polymer matrices as depicted in Fig. 12. The results indicated that the samples without Mn is silent and did not have any responses while those doped with Mn (II) show a typical Mn (II)-EPR pulses of Mn-nano-particles in super-paramagnetic materials. The plotted peak-to-peak intensities show a strong dependency on the primary concentration of the Mn mol.%, which produce linear plot in the range of study (0.1–1.0 Mn mol.%) with good correlation coefficient of 0.9975.

Since the linear calibration curve for a limited range of concentration in this study, the model used to compute the LOD is

$$\text{LOD} = 3 \text{ SD}/b$$  \hspace{1cm} (9)

where $b$ is the calibration plot slope or the line signal intensity ratio of the concentration (concn.). SD is the standard deviation of the y-intercepts of regression lines. This procedure is used here as both of the methods have intercepted approaches zero. Thus, they did not involve a background noise [52,53]. These data produced LOD values of DP-LIBS and EPR systems for manganese to be 0.026 and 0.016 mol.%, respectively.

The DP-LIBS versus EPR data in expression of relative accuracy (RA) is also studied. Accuracy investigates the closeness between...
the recorded values that endorsed, either as a true, typical actual value (i.e., EPR results) and the value observed. In this work, the high precision of the EPR results makes its results the reference value of accurate determination of the Mn element by the DP-LIBS system that was computed using the following equation \[ \text{RA} = \frac{d + SD}{M} \times \frac{f_{\alpha} \times 100}{\varepsilon} \]

where \( M \) is the EPR results as a standard procedure; \( d \) is the difference between the EPR and DP-LIBS results; \( n \) is the number of observations, and \( f_{\alpha} \) is the \( t \)-value at 2.1% error confidence. About ten laser signals have been fired to etch the PVA polymer surface before registering actual data. Also, we stabilized the fluctuation of the laser shots during in situ observations and averaged the DP-LIBS spectra over ten laser pulses. The RSD values should be in the domain of 1–5% for the DP-LIBS geometry \[54\]. The RA of Mn element exists in the PVA polymer for each spiked up concentration is 3.5% relative to the concentration of DP-LIBS and EPR systems, which is acceptable for any perfect instrument.

In addition, the evaluation of Mn line intensities in the polymer by DP-LIBS versus those from EPR results was presented in Fig. 13. The exact correlation recorded between the EPR and DP-LIBS observations show linear regression parameter value \( R^2 = 0.98463 \). While a weak correlation with irregular results recorded between the EPR and SP-LIBS at 266 nm observations show weak linear regression parameter value \( R^2 = 0.67214 \). Hence, the correlation between the EPR and DP-LIBS observations is better than those obtained by SP-LIBS. Therefore, EPR could be utilized to determine Mn and other substances such as N(I), Fe(III), etc., contented in polymer materials.

4. Conclusion

In this work, a high sensitive spectrometer based on collinear double-pulse Nd: YAG lasers ablation and EPR techniques have been exploited for the quantitative and qualitative analysis of various Mn-dopant concentrations in PVA-polymer matrices. The experimental parameters like gate delay \( t_{g} \), the separation distance \( d \) between the lasers focus position and the polymer surface were good optimized for signal enlargement in the DP-LIBS and the EPR schemes. Higher values of plasma density and temperature in DP-LIBS scheme compare to SP-LIBS scheme was observed at the typical values of \( t_{g} \), \( d \) and LPE. The main elements like Mn, C, Li, H and O were detected in our polymer samples. The fingerprint wavelengths of each element and NIST Data base were utilized to identify the spectral assignment. In DP-LIBS system, the good signal enlargement was observed when the 2nd LPE is about 2.5 folds larger than the 1st LPE. Thus, the 2nd laser beam might have longer wavelength compare to the 1st laser beam. On the other hand, the major outcome of the EPR investigations was the Mn-content in the polymer matrices and/or its magnetic property was highly related to nano-paramagnetic particles in the quantum dots range, i.e. 2–5 nm size. The obtained perfect correlation at both systems and their intra-correlation confirm a possibility of DP-LIBS system for monitoring manganese in the polymer as well as other inorganic substances. Therefore, these spectroscopic techniques could be applied for quick analysis of elemental changes inside or on the surface of any matrices.

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