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# Z-Scan measurements of optical nonlinearities for (3GO) dye

Ali H. Al-Hamdani*

*Laser & Optoelectronics Engineering Department, University of Technology, Baghdad, IRAQ.*

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**Abstract**

In this paper a sensitive single-beam technique for measuring both the nonlinear refractive index and nonlinear absorption coefficient for 3GO dye were reported. Descriptions for the experimental details and theoretical analysis including cases where nonlinear refraction is accompanied by nonlinear absorption were presented. In these experiments, the transmittance of a sample is measured through a finite aperture in the far field as the sample is moved along the propagation path (Z) of a focused Gaussian beam. The sign and magnitude of the nonlinear refraction are easily deduced from such a transmittance curve (Z-scan). Employing this technique, the nonlinear refraction is accompanied by nonlinear absorption, it is possible to separately evaluate the nonlinear refraction as well as the nonlinear absorption by performing a second Z scan with the aperture removed. We demonstrate this method for (3GO) dye at 532 nm where two-photon absorption is present and $n_2$ is positive. Also the optical proprieties (absorption, fluorescence spectra and the quantum efficiency) of 3GO dye solution in chloroform with different concentrations were evaluated.

**Keywords**: Z-scan Technique, Nonlinear Refractive Index, Nonlinear absorption coefficient, 3GO dye, Nonlinear optical materials.
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## 1. Introduction

Many applications of the nonlinear optical materials in several photonics devices such as holographic storage, optical amplifiers, optical switching and signal processing is based on the refraction index dependent of illumination intensity [1]. These elements are currently begun performed but there are expectations that they may eventually to be improve their functions with new optical materials. Recently, in several areas of optoelectronics have been huge interests for organic materials because the possibility of optimization of these nonlinearities through manipulation of their composition and aggregation state [2].

There are numerous techniques for the measurement of the linear refractive index [3] and nonlinear refraction index in materials. Nonlinear interferometry [4], degenerate four wave mixing [5], and beam distortion measurements, known as Z-scan [6], are the frequently techniques reported.

The single beam Z-scan analysis, which was developed by Mansoor Sheik Bahae et al. [6], is a simple and effective tool for determining nonlinear optical properties of materials [7-

* ) For correspondence, E-mail: ali_alhamdani2003@yahoo.com

10]. This approach has been now a day widely used in optical characterization of different materials. Nonlinear refractive index is proportional to the real part of the third-order susceptibility Re[$\chi^{(3)}$]. Basically, the Z-scan method consists in translating a nonlinear sample through the focal plane of a tightly focused Gaussian laser beam and monitoring the changes in the far field intensity pattern. For a purely refractive nonlinearity, the light field induces an intensity dependent nonlinear phase and, as consequence of the transverse Gaussian intensity profile, the sample presents a lens-like behavior. The induced self-phase modulation has the tendency of defocusing or recollimating the incident beam, depending on its Z position with respect to the focal plane. By monitoring the transmittance change through a small circular aperture placed at the far field position, it is possible to determine the nonlinear refractive index. In the present study, the nonlinear refractive index ($n_2$) and nonlinear absorption coefficient values $\beta$ were calculated using a single beam Z- scan method. Also the optical proprieties (absorption, fluorescence spectra and the quantum efficiency) of 3GO dye solution in chloroform with different concentrations were evaluated.

## 2. Method of Analysis

The spectrum of the molecular fluorescence F (ύ) gives the relative fluorescence intensity at wave-number (ύ), this is related to the quantum efficiency by the following equation [11,12].

$$q_{fm} = \int_0^\infty F(\upsilon')d\upsilon' \tag{1}$$

In order to evaluate absolute quantum efficiency, we have to consider both the radiative and non-radiative processes taking place in the medium, therefore

$$q_{fm} = \frac{K_{fm}}{K_{fm} + \Sigma K_d} = \frac{K_{fm}}{K_{fm} + K_{IC} + K_{ISC}} \tag{2}$$

Since $K_{fm} = 1/\tau_{fm}$ and $\tau_f = 1/(K_{fm} + \Sigma K_d)$ Therefore,

$$q_{fm} = \frac{\tau_f}{\tau_{fm}} = \int_0^\infty F(\upsilon')d\upsilon' \tag{3}$$

Also $q_{fm} = \frac{Number\ of\ quanta\ emitted}{Number\ of\ quanta\ absorbed}$

Where, $\tau_{fm}$ is the radiation life time can be calculated using relation as follow,

$$\frac{1}{\tau_{fm}} = 2.88*10^{-9} n^2(\nu'^2)\int \varepsilon('\nu)d\nu'. \tag{4}$$

Where, **n** is refractive index of a medium, **ύ** is wave number at the maximum absorption, and ∫ε(ύ)d ύ is the area under the absorption spectrum curve as a function of the wave number [8].

The Z-scan experiments were performed using a 532 nm Nd: YAG (SHG) CW laser beam (COHERENT–Compass 215M-50 diode-pumped laser) focused by a lens of 10 cm focal length. The experimental set up is shown in Fig. 1.

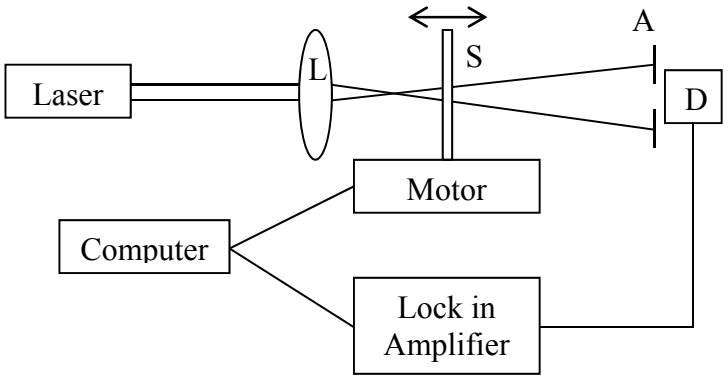


Fig. 1: Schematic diagram of Z-scan experimental setup: L- Lens, S- Sample, A- Aperture, D-Detector.

This normalized transmittance curves are characterized by a pre-focal valley followed by a post-focal peak. This implies that the nonlinear refractive indices of 3GO is positive ($n_2 > 0$). The defocusing effect shown in Z-scan curve can be attributed to a thermal nonlinearity resulting from absorption of radiation at 532 nm. Localized absorption of a tightly focused beam propagating through an absorbing sample medium produces a spatial distribution of temperature in the sample solution and consequently, a spatial variation of the refractive index, that acts as a thermal lens resulting in phase distortion of the propagating beam.

The nonlinear refractive index ($n_2$) is calculated using the standard relations [18].

$$\Delta T_{P-V} = 0.406(1-S)^{0.25}|\Delta\varphi_0| \tag{5}$$

Where $\Delta T_{p-v}$ can be defined as the difference between the normalized peak and valley transmittances ($T_P$-$T_V$), $|\Delta\varphi|$ is the on-axis phase shift at the focus.
The linear transmittance of the aperture is given by,

$$S = 1 - \exp(-\frac{2r_a^2}{\omega_a^2}) \tag{6}$$

where $r_a$ is the radius of the aperture and $\omega_a$ is the beam radius at the aperture.
The nonlinear refractive index $n_2$ is,

$$n_2 \approx \frac{\Delta\varphi_0}{kI_0L_{eff}} \tag{7}$$

where k is the wave number $(2\pi/\lambda)$ and $L_{eff} = \frac{1-e^{-\propto_0 L}}{\propto_0}$, L, is the thickness of the sample, $\alpha_0$ is the linear absorption coefficient, which can be found from transmission spectrum of the sample from the following formula $\propto_0 = \frac{1}{t} ln \frac{1}{T}$, where, t is the thickness of sample and T is transmittance.

$I_0 = \frac{2P}{\pi\omega_{0r}^2}$ is defined as the peak on-axis irradiance at the focus.

Where, $w_{or}$ is the beam radius at the focus and P is the power of the laser beam.

An open-aperture z-scan measures the change in power intensity of a beam, focused by the lens in Fig. 1 in the far field at detector, which captures the entire beam. The change in power intensity is caused by multi-photon absorption in the sample as it travels through the beam waist. In the focal plane where the intensity is greatest, the largest nonlinear absorption is observed. At the "tails" of the z-scan signature, where z | >> Raleigh range ($z_o$), the beam intensity is too weak to elicit nonlinear effects. The higher order of multi-photon absorption present in the measurement depends on the wavelength of light and the energy levels of the sample [14]. Clearly, even with nonlinear absorption, a Z-scan with a fully open aperture is insensitive to nonlinear refraction of the sample. The Z-scan traces with no aperture are expected to be symmetric with respect to the focus (Z=0) where they have a minimum transmittance (e.g., multi-photon absorption) or maximum transmittance (e.g., saturation of absorption).

In fact, the coefficients of nonlinear absorption $\beta$ can be easily calculated from such transmittance curves [12, 15].
The maximum transmittance (T(Z)) is given by [16];

$$T(Z) = 1 - \frac{I_o L_{eff}\, \beta[1+Z]}{2\sqrt{2}} \tag{8}$$

Where Z is the sample position at the maximum transmittance.

## 3. Experimental Procedure

The measurements of the absorption and fluorecence spectra of the samples are taken by using a spectrophotometer (Metertech, SP8001, UV/VIS Spectrophotometer), and the emission spectra taken by using (Spectrofluorometer-model SL174, Elico) respectively. Refractive index is measured by using refractometer (Bellingham and Stanley Ltd, Tunbridgewells, ABBE60, England). Different concentrations ($1*10^{-5}$, $2*10^{-5}$, $5*10^{-5}$, $7*10^{-5}$ and $1*10^{-4}$ mol/l) of 3GO dye dissolved in diachloform were prepared at the laboratory environments.

## 4. Results and Discussion

Fig. 2, shows the absorption and fluorescence spectra for liquid solution of 3GO dye dissolved in chloroform $CHCL_3$ solvent. From this figure, the position of the maximum sample absorption and maximum fluorescence are indicated.

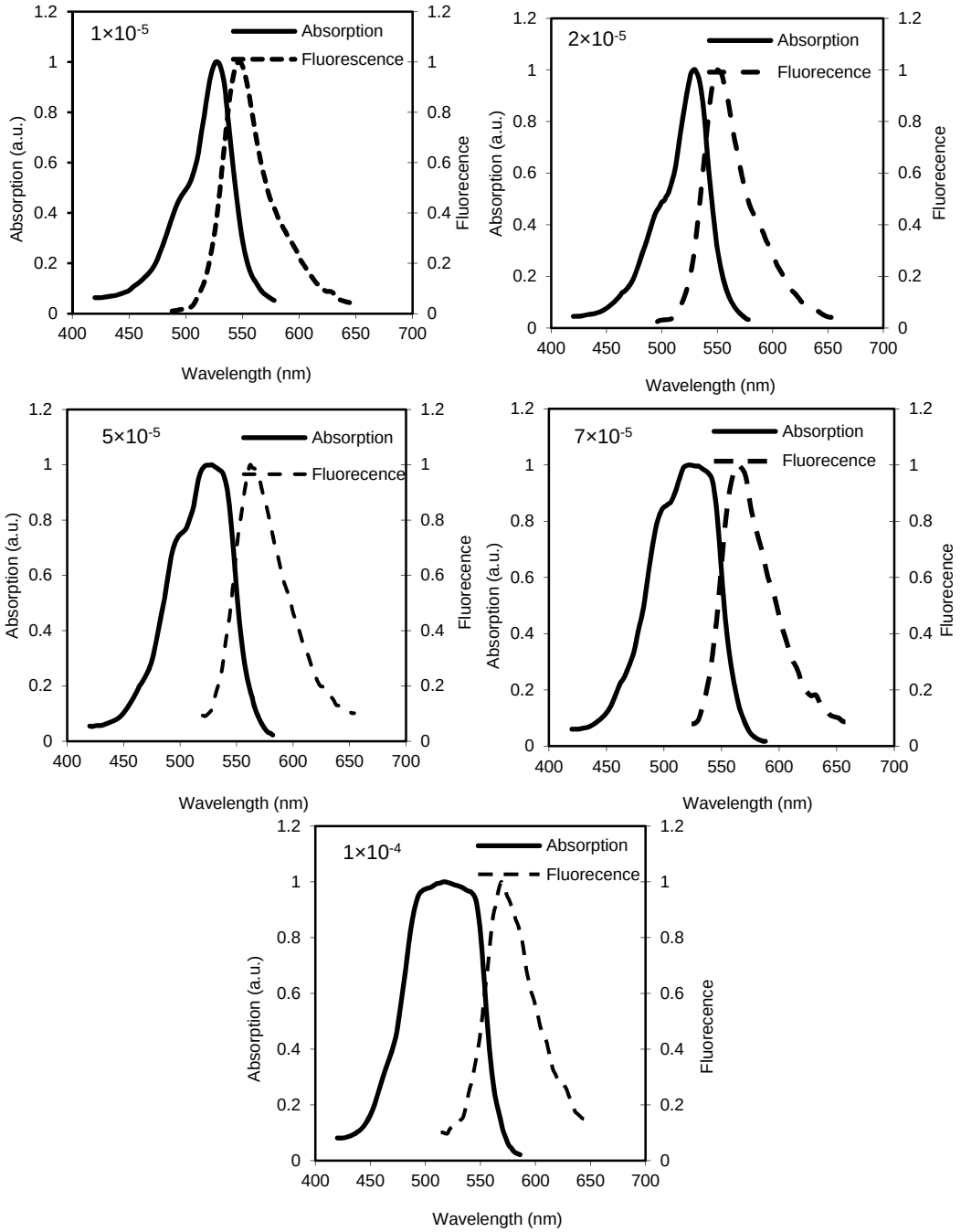


Fig. 2: The fluorescence and absorption spectra for 3GO dye dissolved in chloroform with different concentration ($1*10^{-5}$, $2*10^{-5}$, $5*10^{-5}$, $7*10^{-5}$ and $1*10^{-4}$ mol/l).

The stock shift which represent the difference between the positions of the peak fluorescence ($\lambda_{Fluo.max)}$ and peak absorption ($\lambda_{Abs.max)}$ of the dye at each concentrations are summarized in Table 1, which also include the values of quantum efficiencies, the fluorescence life time (Equations 1-3). From the table it is shown that as the 3GO dye increased the stock shift and the quantum efficiency is increased.

Table 1: Optical properties of 3GO dye dissolved in chloroform [17].

| Concentration Mol/l | Absorption ($\lambda_{Abs.max}$) | Fluorescence ($\lambda_{Fluo.max}$) | Stock Shift nm | Quantum Efficiency % | $K_{fm}$ | $\tau_{fm}$ | $\tau_f$ |
|---|---|---|---|---|---|---|---|
| $1*10^{-5}$ | 528 | 550 | 22 | 0.95 | 4.573418 | 0.218654 | 0.207722 |
| $2*10^{-5}$ | 528 | 557 | 29 | 0.97 | 2.013924 | 0.496543 | 0.481646 |
| $5*10^{-5}$ | 530 | 569 | 39 | 0.95 | 0.830098 | 1.204676 | 1.144442 |
| $7*10^{-5}$ | 530 | 574 | 44 | 0.81 | 0.660703 | 1.513537 | 1.225965 |
| $1*10^{-4}$ | 524 | 578 | 54 | 0.68 | 0.650974 | 1.536158 | 1.044587 |

The nonlinear refractive index and nonlinear absorption coefficient of 3GO dissolved in chloroform were measured by the Z-scan techniques. The sample thickness was 1 mm. Two techniques had been used to measure the nonlinear optical properties of 3GO, closed-aperture which was used to measure the nonlinear refractive index and open- aperture which was used to measure the nonlinear absorption coefficient.

In order to investigate the nonlinear refractive index, closed-aperture z-scan technique shown in Fig. 1 was used. Fig. 3 shows the closed-aperture Z-scan curves, by using 532 nm laser, this figure represents the normalized transmittance as a function of sample position (Z).

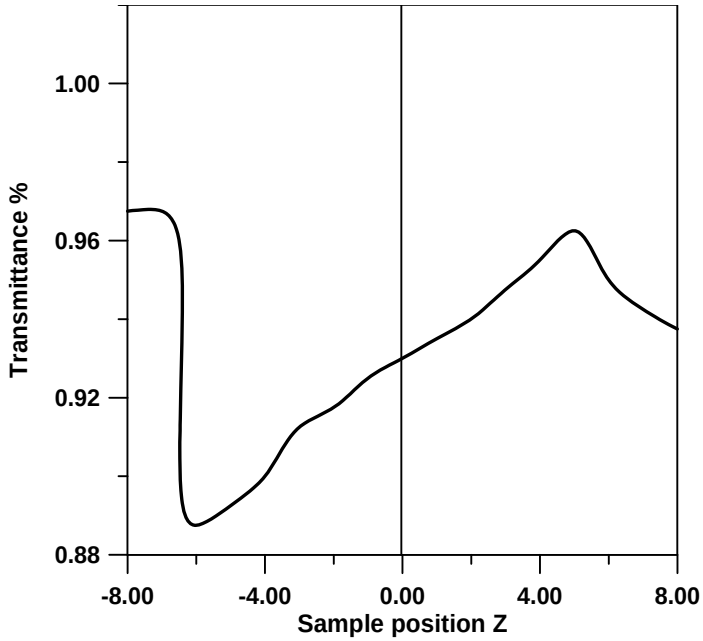


Fig. 3: Closed Z-scan of 1 mm thick 3GO cell using a frequency doubled Nd:YAG laser λ=532 nm.

From the figure (3), the normalized transmittance started with low change (linear) at different positions from the far field of the sample position (-Z) with respect to the focal plan at Z=0. At the near field the transmittance begins to decrease until it reaches the minimum value (Tv) at approximately Z=-6 mm. After the focal plane, the normalized transmittance begins to increase until it reaches the maximum value (Tp) at approximately Z=5. The normalized transmittance begins to decrease toward a low change behavior at the far field of the sample position +Z, the closed- aperture Z-scan measures the transmittance of a sample, as it passes through the focal plan. The sample nonlinearity was calculated from the difference between the heights (peak) and the lowest value (valley) transmission ($\Delta T_{P-V}$). Table 2, shows the nonlinear refractive index calculated from equations (8).

The nonlinear absorption coefficient $\beta$ of the samples was determined by performing the open aperture Z-scan. Fig. 4 shows the open- aperture Z-scan curves, which represents the normalized transmission as function of position Z.

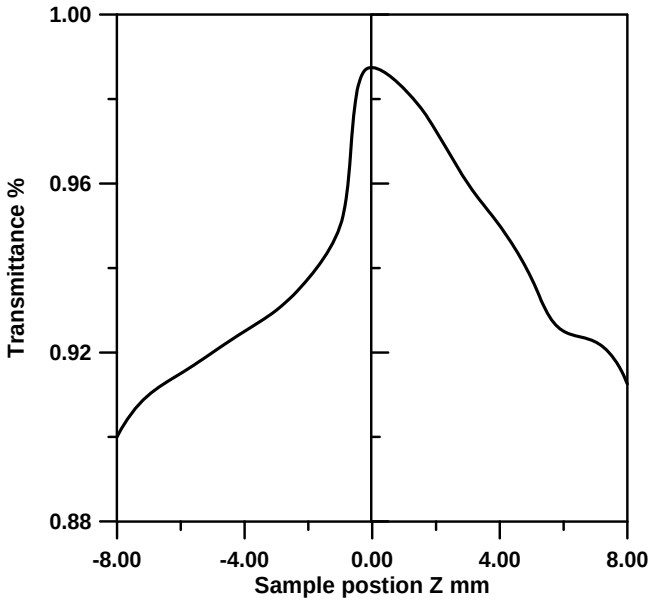


Fig. 4: Open Z-scan of 1 mm thick 3GO cell using a frequency doubled Nd:YAG laser λ=532 nm.

From Fig. 4 the behavior of transmittance curves starts linearly at different distances from the far field of the sample position (-Z). The near fold the transmittance curve begins to increase until it reaches the maximum value ($T_{max}$) at the focal print, where (Z=0 mm), afterwards, the transmittance begins to decrease toward the linear behavior at the far field of the sample position (+Z), from the open aperture Z-scan data, the nonlinear absorption coefficient is estimated by using equation (8) and its value was $1.078*10^{-13}$ m/W and the maximum transmittance was 0.9875.

Table 2: Nonlinear optical properties of 3GO dye measured at 532 nm laser beam.

| **Parameters** | **Value** |
|---|---|
| Transmittance T% | 27.176 |
| Linear absorption coefficient ($\alpha_{0)}$ cm-$^{1}$ | 0.1302 |
| Linear refractive index ($n_{0)}$ | 1.477 |
| Peak laser irradiance ($I_{0)}$ mW/cm$^2$ | 1732.48 |
| on-axis phase shift (ΔΦ) rad | 0.1847 |
| $L_{eff}$ (cm) | 0.937 |
| Non-linear absorption coefficient (ß) cm$^2$/mw | 2,156*10-$^{5}$ |
| Non-linear refractive index ($n_2$ ) cm$^2$/mW | $6.344*10^{-7}$ |

## 5. Conclusions

There are a variety of methods and techniques for determine the nonlinear optical response each with its own weakness and advantages in general, it is advisable to use as many complementary techniques as possible over a broad spectral range in order to unambiguously determine the active nonlinearities. The simplicity and sensitivity of the technique described here make it attractive as a screening test to give the sign, magnitude, and order of the nonlinear response of new nonlinear-optical materials.

## References

[1] C. Yeh, Applied photonics, Academic Press. San Diego (1994)
[2] Weifeng, Wenhui Yi, Hongcai Wu, Ozaki Masanori, Yoshino Katsumi, Journal of Applied Physics, **98**(3) (2005) 034301
[3] M. J. Moran, C. Y. She, R. L. Carman, IEEE Journal of Quantum Electronics, **11** (1975) 259
[4] S. K. J. Al-Ani, G. A. A. Aldaby, F. M. Thabet, Int. J. Nanoelectronics and Materials, **4** (2011)145
[5] S. R. Friberg, P. W. Smith, IEEE Journal of Quantum Electronics, **23** (1987) 2089
[6] M. Sheik Bahae, A. A. Said, T. H., Wei, D. J. Hagan, E. W. Vanstryland, Quantum Electron, **26** (1990) 760
[7] M. A, Qusay, P. K. Palanisamy, Optik, **116** (2005) 515
[8] R. Madhanasundari, P. K. Palanisamy, Modern Physics Letter B, **20** (2006) 887
[9] M. A. Qusay, P. K. Palanisamy, Modern Physics Letter B, **20** (2006) 623
[10] A. N. Dhinaa, Y. N. Ahmad, P. K. Palanisamy, Journal of nonlinear Optical Physics and Materials, **16** (2007) 359
[11] F. Lee Rodkly, Archives of Biochemistry and Biophysics, **108** (1964) 510
[12] W. T. Caraway, C. W. Kammeyer, Clinica Chimica Acta, **41** (1972) 395
[13] M. P. Elking, H. F. Kabat, American Journal of Hospital Pharmacy, **25** (1968) 485
[14] S. L. G´omez, F. L. S. Cuppo, A. M. Figueiredo Neto, Brazilian Journal of Physics, **33** (2003)
[15] K. Kandasamy, K. D. Rao, R. Deshpande, P. N. Puntambekar, B. P. Singh, S. J. Shetty, T. S. Srivastava, Journal of Applied Physics B: Lasers and Optics, **64**(4) (1997) 479
[16] J. C. Torres, J. Hernandez , S. G. Martinez, A. A. Lopez, M. B. Hernandez, J. A. Aguilar-Martne, Mexicana Physical Review, **52**(6) (2006) 540
[17] Ali H. Al-Hamdani, Yasmeen Z. Dawood, Safaa M. Jasim, *Spectral Properties of Liquid samples of Rodamine( 3GO ) dye Disolved in Chloroform*, to be published in Engineering & Technology Journal, (2012)