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**EXPERIMENTAL UNCERTAINTY IN THIRD-ORDER  
SUSCEPTIBILITY AND MOLECULAR SECOND  
HYPERPOLARIZABILITY MEASUREMENTS OBTAINED WITH  
DEGENERATE FOUR-WAVE MIXING**

By

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## PREFACE

This report summarizes the development and application of an analysis of the uncertainty in third-order susceptibility and second hyperpolarizability measurements obtained experimentally with degenerate four-wave mixing. This work is being done under the project Laser Eye Protection, 5325006CA0A00, administered by the Technology Application Branch, Fiber and Polymer Science Division, Science and Technology Directorate, U.S. Army Soldier Systems Command, Natick Research, Development, and Engineering Center.

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EXPERIMENTAL UNCERTAINTY IN THIRD-ORDER SUSCEPTIBILITY  
AND MOLECULAR SECOND HYPERPOLARIZABILITY MEASUREMENTS  
OBTAINED WITH DEGENERATE FOUR WAVE MIXING

INTRODUCTION

Third-order susceptibility and molecular second hyperpolarizability measurements are currently performed with degenerate four-wave mixing (DFWM). Experimental values obtained by this technique have been reported with estimated confidence intervals. This report describes an uncertainty analysis that can be used to 1) better define experimental uncertainties, 2) add some insight into the degree to which individual experimental parameters affect overall system accuracy, and 3) validate comparisons of experimental  $\chi^{(3)}$  and  $\langle \gamma \rangle$  values for various compounds to confirm the significance of any observed variations in nonlinear response, as in the study of trends.

The DFWM system described here utilizes a backward-beam geometry where two strong collinear pump beams, propagating in opposite directions, interact at the sample with a third less-intense probe beam to create a fourth nonlinear optical phase conjugate beam. The intensity of the conjugate signal is proportional to the square of the  $\chi^{(3)}$  of the sample under study. The signal is measured with a silicon photodiode and oscilloscope. It is then compared to a similar signal obtained from a carbon disulfide standard under identical conditions using the expression

$$\frac{\chi^{(3)}_{\text{sample}}}{\chi^{(3)}_{\text{CS}_2}} = \left( \frac{n_{\text{sample}}}{n_{\text{CS}_2}} \right)^2 \frac{d\alpha}{1 - e^{-\alpha d}} e^{\alpha d/2} \left( \frac{I_{\text{sample}}}{I_{\text{CS}_2}} \right)^{1/2} \frac{d_{\text{CS}_2}}{d_{\text{sample}}} \dots \quad (1)$$

where  $n$  is the index of refraction,  $\alpha$  is the linear absorption coefficient,  $d$  is the length of the sample and  $I$  is the measured signal of the phase conjugate beam. This approach eliminates the need of obtaining absolute irradiance measurements for each of the additional three beams used in the DFWM setup.<sup>1</sup>

The relationship between the molecular second hyperpolarizability  $\langle \gamma \rangle$  and the third-order macroscopic susceptibility of the solute is given by the expression

$$\langle \gamma \rangle = \frac{\chi^{(3)}}{L^4 N} \quad (2)$$

where  $N$  is the number density of molecules per mL and

$$L = \frac{n^2 + 2}{3}. \quad (3)$$

It is generally assumed that the conjugate signal is due to a combination of third-order nonlinearities in both the solvent and solute and that for a solution of noninteracting particles the relationship is additive:<sup>1</sup>

$$\chi^3_{\text{solution}} = L^4 [N_{\text{solvent}} \gamma_{\text{solvent}} + N_{\text{solute}} \gamma_{\text{solute}}] \dots \quad (4)$$

The  $\chi^{(3)}_{\text{solution}}$  is obtained experimentally with Eq. 1. For nonsaturated solutions

$$N_{\text{solute}} = \frac{A C}{M} \quad (5)$$

where  $A$  is Avogadro's number,  $M$  is the molecular weight of the solute, and  $C$  is the concentration. Making appropriate substitutions of Eqs. 2 and 5 into Eq. 4, the following expression is obtained:

$$\chi^3_{\text{solution}} = \chi^3_{\text{solvent}} + (L^4 \gamma_{\text{solute}} A/M) C. \quad (6)$$

By evaluating Eq. 1 for a series of dilute solutions and plotting the results versus respective concentration, a straight line is obtained. A least-squares approximation is then applied to the data from which one obtains  $\chi^{(3)}_{\text{solvent}}$  from the y-intercept and  $\gamma_{\text{solute}}$  from the slope. The  $\chi^{(3)}_{\text{solute}}$  is then obtained from Eq. 2.

## DERIVATION OF UNCERTAINTY EQUATIONS

If it is assumed that the uncertainties ( $W_1, W_2, \dots, W_n$ ) in the independent variables ( $X_1, X_2, \dots, X_n$ ) are all given with the same probability, then the uncertainty ( $W_R$ ) in the dependent variable ( $R$ ) is given by the expression

$$W_R = \left[ \left( \frac{\partial R}{\partial X_1} W_1 \right)^2 + \left( \frac{\partial R}{\partial X_2} W_2 \right)^2 + \dots + \left( \frac{\partial R}{\partial X_n} W_n \right)^2 \right]^{1/2} \quad (7)$$

By inserting Eq. 1 into Eq. 7 a probable estimate of the uncertainty in experimentally determined  $\chi^{(3)}_{\text{sample}}$  is obtained:

$$W_{\chi^{(3)}_s} = \left[ \left( \frac{\partial \chi^{(3)}_s}{\partial \chi^{(3)}_R} W_{\chi^{(3)}_R} \right)^2 + \left( \frac{\partial \chi^{(3)}_s}{\partial I_s} W_{I_s} \right)^2 + \left( \frac{\partial \chi^{(3)}_s}{\partial I_R} W_{I_R} \right)^2 + \left( \frac{\partial \chi^{(3)}_s}{\partial n_s} W_{n_s} \right)^2 + \left( \frac{\partial \chi^{(3)}_s}{\partial n_R} W_{n_R} \right)^2 + \left( \frac{\partial \chi^{(3)}_s}{\partial d_R} W_{d_R} \right)^2 + \left( \frac{\partial \chi^{(3)}_s}{\partial d_s} W_{d_s} \right)^2 + \left( \frac{\partial \chi^{(3)}_s}{\partial \alpha} W_{\alpha} \right)^2 \right]^{1/2} \quad (8)$$

where

$$\frac{\partial \chi^{(3)}_s}{\partial \chi^{(3)}_R} = \left( \frac{I_s}{I_R} \right)^{1/2} \left( \frac{n_s}{n_R} \right)^2 \left( \frac{d_R}{d_s} \right) \frac{\alpha L}{(1-e^{-\alpha L})} e^{\alpha L/2}, \quad (9)$$

$$\frac{\partial \chi^{(3)}_s}{\partial I_s} = \frac{\chi^{(3)}_R}{2\sqrt{I_s I_R}} \left( \frac{n_s}{n_R} \right)^2 \left( \frac{d_R}{d_s} \right) \frac{\alpha L}{(1-e^{-\alpha L})} e^{\alpha L/2}, \quad (10)$$

$$\frac{\partial \chi^{(3)}_s}{\partial I_R} = \frac{-\chi^{(3)}_R}{2} \frac{(I_s)^{1/2}}{(I_R)^{3/2}} \left( \frac{n_s}{n_R} \right)^2 \left( \frac{d_R}{d_s} \right) \frac{\alpha L}{(1-e^{-\alpha L})} e^{\alpha L/2}, \quad (11)$$

$$\frac{\partial \chi^{(3)}_s}{\partial n_s} = \chi^{(3)}_R \left( \frac{I_s}{I_R} \right)^{1/2} \left( \frac{2n_s}{n_R^2} \right) \left( \frac{d_R}{d_s} \right) \frac{\alpha L}{(1-e^{-\alpha L})} e^{\alpha L/2}, \quad (12)$$

$$\frac{\partial \chi^{(3)}_s}{\partial n_R} = \chi^{(3)}_R \left( \frac{I_s}{I_R} \right)^{1/2} \left( \frac{-2n_s^2}{n_R^3} \right) \left( \frac{d_R}{d_s} \right) \frac{\alpha L}{(1-e^{-\alpha L})} e^{\alpha L/2}, \quad (13)$$

$$\frac{\partial \chi^{(3)}_S}{\partial d_R} = \chi^{(3)}_R \left( \frac{I_S}{I_R} \right)^{1/2} \left( \frac{n_S}{n_R} \right)^2 \left( \frac{1}{d_S} \right) \frac{\alpha L}{(1-e^{-\alpha L})} e^{\alpha L/2}, \quad (14)$$

$$\frac{\partial \chi^{(3)}_S}{\partial d_S} = \chi^{(3)}_R \left( \frac{I_S}{I_R} \right) \left( \frac{n_S}{n_R} \right)^2 \left( \frac{-d_R}{d_S^2} \right) \frac{\alpha L}{(1-e^{-\alpha L})} e^{\alpha L/2}, \quad (15)$$

and

$$\frac{\partial \chi^{(3)}_S}{\partial \alpha} = \chi^{(3)}_R \left( \frac{I_S}{I_R} \right)^{1/2} \left( \frac{n_S}{n_R} \right)^2 \left( \frac{d_R}{d_S} \right) \frac{(1-e^{-\alpha L}) \left[ L \left( \frac{\alpha L}{2} + e^{\alpha L/2} \right) \right] - \alpha L^2 e^{-\alpha L/2}}{(1-e^{-\alpha L})^2}. \quad (16)$$

Similarly, for the uncertainty in  $\langle \gamma \rangle$ , Eq. 2 is applied to Eq. 7 to obtain:

$$W_\gamma = \left[ \left( \frac{\partial \gamma}{\partial \chi^{(3)}} W_{\chi^{(3)}} \right)^2 + \left( \frac{\partial \gamma}{\partial M} W_M \right)^2 + \left( \frac{\partial \gamma}{\partial L} W_L \right)^2 + \left( \frac{\partial \gamma}{\partial A} W_A \right)^2 \right]^{1/2}, \quad (17)$$

where

$$\frac{\partial \gamma}{\partial \chi^{(3)}} = \frac{M}{L^4 A}, \quad (18)$$

$$\frac{\partial \gamma}{\partial M} = \frac{\chi^{(3)}}{L^4 A}, \quad (19)$$

$$\frac{\partial \gamma}{\partial L} = \frac{-4\chi^{(3)}M}{L^5 A}, \quad (20)$$

and

$$\frac{\partial \gamma}{\partial A} = 0 \quad (\text{assumed}). \quad (21)$$

In order to evaluate Eq. 8, absolute error values are required for  $\chi^{(3)}_R$ ,  $I_S$ ,  $I_R$ ,  $n_S$ ,  $n_R$ ,  $d_R$ ,  $d_S$ , and  $\alpha$ . These can all be determined directly through

experimental considerations or can be given assumed values. For Eq. 17 error values for  $M$ ,  $\chi^{(3)}$  (solute), and  $L$  must be obtained. Additional calculations must be performed to obtain estimates for the uncertainty in  $\chi^{(3)}$  (solute), and  $L$ . For  $W_L$ , Eqs 3 and 7 are combined:

$$W_L = \left[ \left( \frac{\partial L}{\partial n_s} W_{n_s} \right)^2 \right]^{1/2}, \quad (22)$$

where

$$\frac{\partial L}{\partial n_s} = \frac{2n_s}{3}. \quad (23)$$

For the uncertainty in  $\chi^{(3)}$ , Eq. 6 is first written in the form:

$$\chi^{(3)}_{slt} = \frac{(\chi^{(3)}_s - \chi^{(3)}_{slv}) (1000)}{C}. \quad (24)$$

The factor of 1000 is included as a dimensional constant. Applying Eq. 7:

$$W_{\chi^{(3)}_{slt}} = \left[ \left( \frac{\partial \chi^{(3)}_{slt}}{\partial \chi^{(3)}_s} W_{\chi^{(3)}_s} \right)^2 + \left( \frac{\partial \chi^{(3)}_{slt}}{\partial \chi^{(3)}_{slv}} W_{\chi^{(3)}_{slv}} \right)^2 + \left( \frac{\partial \chi^{(3)}_{slt}}{\partial C} W_C \right)^2 \right]^{1/2}, \quad (25)$$

where

$$\frac{\partial \chi^{(3)}_{slt}}{\partial \chi^{(3)}_s} = \frac{1000}{C}, \quad (26)$$

$$\frac{\partial \chi^{(3)}_{slt}}{\partial \chi^{(3)}_{slv}} = \frac{-1000}{C}, \quad (27)$$

and

$$\frac{\partial \chi^{(3)}_{slt}}{\partial \chi^{(3)}_{slv}} = 1000 \left( \frac{\chi^{(3)}_s - \chi^{(3)}_{slv}}{C^2} \right). \quad (28)$$

The value of  $W_c$  depends upon the method with which the solutions are prepared. The technique currently being used relies on accurate weight measurements to determine the solution concentration. Briefly, an initial concentration ( $C_i$ ) is prepared using a precision balance for the solute and a volumetric flask for the solvent. For each run a portion of the solution is used. After each run the mass of the remaining solution is determined ( $m_f$ ). The flask is again filled and weighed to obtain the initial weight of the next run ( $m_n$ ). Using the following expression the new concentration is obtained (see Appendix A for derivation):

$$C_n = C_i \frac{m_f}{m_n}. \quad (29)$$

Advantages of this technique include ease of weight measurements, a reduction in waste solvent, and high overall accuracy. To obtain  $W_c$  we evaluate the following equation:

$$W_{C_n} = \left[ \left( \frac{\partial C_n}{\partial C_i} W_{C_i} \right)^2 + \left( \frac{\partial C_n}{\partial m_f} W_{m_f} \right)^2 + \left( \frac{\partial C_n}{\partial m_n} W_{m_n} \right)^2 \right]^{1/2}, \quad (30)$$

where

$$\frac{\partial C_n}{\partial C_i} = \frac{m_f}{m_n}, \quad (31)$$

$$\frac{\partial C_n}{\partial m_f} = \frac{C_i}{m_n}, \quad (32)$$

and

$$\frac{\partial C_n}{\partial m_n} = \frac{-C_i m_f}{m_n^2}. \quad (33)$$

In order to evaluate Eq. 30 a value for  $W_{C_i}$  must be estimated. Beginning with the expression

$$C_i = \frac{m_i}{V_i}, \quad (34)$$

where  $m_i$  is the initial weight and  $V_i$  is the initial volume, we must evaluate the following equation:

$$W_{C_i} = \left[ \left( \frac{\partial C_i}{\partial m_i} W_{m_i} \right)^2 + \left( \frac{\partial C_i}{\partial V_i} W_{V_i} \right)^2 \right]^{1/2}, \quad (35)$$

where

$$\frac{\partial C_i}{\partial m_i} = \frac{1}{V_i}, \quad (36)$$

and

$$\frac{\partial C_i}{\partial V_i} = \frac{-m_i}{V_i^2}. \quad (37)$$

These expressions have been incorporated into a computer program (Appendix B) which calculates  $\chi^{(3)}_{\text{solution}}$ ,  $\chi^{(3)}_{\text{solute}}$ , and  $\langle \gamma \rangle_{\text{solute}}$  and the uncertainties associated with each of these values.

### EXPERIMENTAL-PARAMETER SENSITIVITY

In order to evaluate the uncertainty equations that were derived in the previous section, values are assumed for the absolute errors of the independent variables. These are given as percent errors in Table 1.

Table 1. Assumed percent errors for experimental parameters

<u>Parameter</u>	<u>Assumed Percent Error</u>
$\chi^{(3)}_{CS_2}$	0%
$I_{\text{solution}}$	5%
$I_{CS_2}$	5%
$n_{\text{solution}}$	1%
$n_{CS_2}$	0.1%
$d_{\text{sample}}$	0.1%
$d_{CS_2}$	0.1%
$\alpha_{\text{solution}}$	0.08%
$M_{\text{solute}}$	0.1%
$mass_{\text{solution}}$	1%
$volume_{\text{solution}}$	1%

It is assumed that an exact value for  $\chi^{(3)}_{CS_2}$  is known. Uncertainties in intensity measurements are based on an estimate of the readability of the oscilloscope used in the evaluations. The index of refraction for  $CS_2$  is considered more accurate than that of the sample because it is assumed that  $n_{\text{solution}} = n_{\text{solvent}}$ , and additional error is allowed here. Percent errors given for the cell thicknesses  $d_{\text{sample}}$  and  $d_{CS_2}$  are manufacturer stated tolerances. Mass and volume tolerances are based on scale readabilities.

Absolute errors for solution concentrations are calculated using Eq. 30. These will slightly increase with each new solution that is prepared. For example, for an initial concentration of 1 mg/mL, where 0.005 g of solute is dissolved in 5 mL of solvent with tolerances of  $\pm 0.0001$  g and  $\pm 0.05$  mL, respectively, Eq. 35 gives an uncertainty of 0.00002 g/mL or 2.2% for the initial concentration. This value is then used as input into Eq. 30 to obtain the uncertainty in the following, more dilute solution. Table 2 shows an example in which each consecutive concentration is half the previous concentration. New concentrations ( $C_n$ ) are calculated at the end of each run using the mass measurements shown for that run and Eq. 29. Absolute uncertainties ( $W_{Cn}$ ) are predicted with Eq. 30 and percent errors are also shown for each run.

Table 2. Uncertainty in concentration measurements for a standard run.

$C_i$ (g/mL)	$m_i$ (g)	$m_f$ (g)	$m_n$ (g)	$C_n$ (g/mL)	$W_{Cn}$ (g/mL)	% Error
$1 \times 10^{-3}$	4.6	2.3	4.6	$5 \times 10^{-4}$	$1 \times 10^{-5}$	1%
$5 \times 10^{-4}$	4.6	2.3	4.6	$2.5 \times 10^{-4}$	$5 \times 10^{-6}$	1%
$2.5 \times 10^{-4}$	4.6	2.3	4.6	$1.25 \times 10^{-4}$	$4 \times 10^{-6}$	1.6%
$1.25 \times 10^{-4}$	4.6	2.3	4.6	$6.25 \times 10^{-5}$	$2 \times 10^{-6}$	1.6%
$6.25 \times 10^{-5}$	4.6	2.3	4.6	$3.12 \times 10^{-5}$	$1 \times 10^{-6}$	1.6%

These values are used as input to program ERRCHI-3.BAS. Table 3 gives additional input for a representative run where the  $\chi^{(3)}$  of zinc tetraphenyl tetrabenzporphyrin in tetrahydrofuran was evaluated.

Table 3. ERRCHI-3.BAS input data for experimental run of zinc tetraphenyl tetrabenzporphyrin in tetrahydrofuran.

<u>Variable</u>	<u>Input</u>
$I_{\text{solution}}$	28000
$I_{\text{CS2}}$	150000
$\alpha$	0.875
$C_i$	0.00076 g/mL
$\chi^{(3)}_{\text{solvent}}$	$2.4 \times 10^{-14}$ esu
$W_{\chi^{(3)}_{\text{solvent}}}$	$9.7 \times 10^{-16}$ esu
M	678
weight	0.0038 g
vol	5 mL

The following output was obtained for this run:

$\chi^{(3)}$  of solution =  $1.45 \times 10^{-12}$   
 Uncertainty =  $5.94 \times 10^{-14}$   
 Percent Error = 4%

$\chi^{(3)}$  of solute =  $1.88 \times 10^{-9}$   
 Uncertainty =  $7.85 \times 10^{-11}$   
 Percent Error = 4%

$\langle \gamma \rangle$  of solute =  $6.3 \times 10^{-31}$

Uncertainty =  $3.64 \times 10^{-32}$

Percent Error = 6%

Uncertainty in  $\chi^{(3)}_{\text{solution}}$  due to:

$$\chi^{(3)}_{\text{CS}_2} = 0$$

$$\text{Voltage reading for solution} = 3.6 \times 10^{-14}$$

$$\text{Voltage reading for CS}_2 = 3.6 \times 10^{-14}$$

$$\text{Solution refractive index} = 2.9 \times 10^{-14}$$

$$\text{CS}_2 \text{ refractive index} = 2.9 \times 10^{-15}$$

$$\text{Solution cell thickness} = 1.5 \times 10^{-15}$$

$$\text{CS}_2 \text{ cell thickness} = 1.5 \times 10^{-15}$$

$$\text{Sample absorption} = 5.4 \times 10^{-16}$$

Uncertainty in concentration due to:

$$\text{Weight} = 0.0076$$

$$\text{Volume} = 0.0076$$

Uncertainty in  $\chi^{(3)}_{\text{solute}}$  due to:

$$\chi^{(3)}_{\text{solution}} = 7.8 \times 10^{-11}$$

$$\chi^{(3)}_{\text{solvent}} = 1.3 \times 10^{-11}$$

$$\text{Concentration} = 2.7 \times 10^{-11}$$

Uncertainty in field factor due to:

$$\text{Solution refractive index} = 0.014$$

Uncertainty in  $\langle \gamma \rangle$  due to:

$$\chi^{(3)}_{\text{solute}} = 2.7 \times 10^{-32}$$

$$\text{Molecular weight} = 6.3 \times 10^{-34}$$

$$\text{Field factor (L)} = 2.5 \times 10^{-32}$$

The value for  $\chi^{(3)}_{\text{solvent}}$  and its corresponding uncertainty was obtained by first running the program at zero concentration. Uncertainties due to individual experimental parameters shown above are obtained from the product of the parameter sensitivity and its absolute uncertainty, for instance, from Eq. 7:

$$\frac{\partial R}{\partial X_1} w_1. \quad (38)$$

These values show the relative degree to which single variables contribute to the overall uncertainty. For example, the greatest degree of uncertainty in the experimental value for  $\chi^{(3)}_{\text{solution}}$  is due to oscilloscope voltage readings.

A similar output to that shown above is obtained for each concentration evaluated in the series. Each value of  $\chi^{(3)}_{\text{solution}}$ ,  $\chi^{(3)}_{\text{solute}}$ , and  $\langle \gamma \rangle$  will have an associated uncertainty based on the values of the experimental parameters unique to that run. The final values reported for  $\chi^{(3)}_{\text{solution}}$ ,  $\chi^{(3)}_{\text{solute}}$ , and  $\langle \gamma \rangle$  are obtained via a curve fitting technique while their respective uncertainties are obtained by taking the sample standard deviation of the individual uncertainties obtained for each run.

In some instances the input uncertainties given in Table 1 may vary; for example, in a case where the sample is in the form of a thin film, the thickness of which can only be approximated. With this in mind a series of plots were generated which show the change in the uncertainty of  $\chi^{(3)}_{\text{solute}}$  and  $\langle \gamma \rangle$  resulting from an increase in the uncertainty of a single variable. These are shown in Appendix C, Figs. C1-C21. In each plot the uncertainty in a single independent variable has been increased from 0% to 50% error while the uncertainty in the remaining independent variables has been kept constant at the current values.

The series of sensitivity plots for both  $\chi^{(3)}_{\text{solute}}$  and  $\langle \gamma \rangle$  are summarized in the following bar charts where the normalized average slope of each variable is shown. The charts show the relative degree to which a given variable is sensitive to changes in percent error. For example, the uncertainty in  $\chi^{(3)}_{\text{solute}}$  is most sensitive to uncertainty in the refractive indices of both  $\text{CS}_2$  and the solution while accuracy in determining the linear absorption of the sample has a minimal effect.

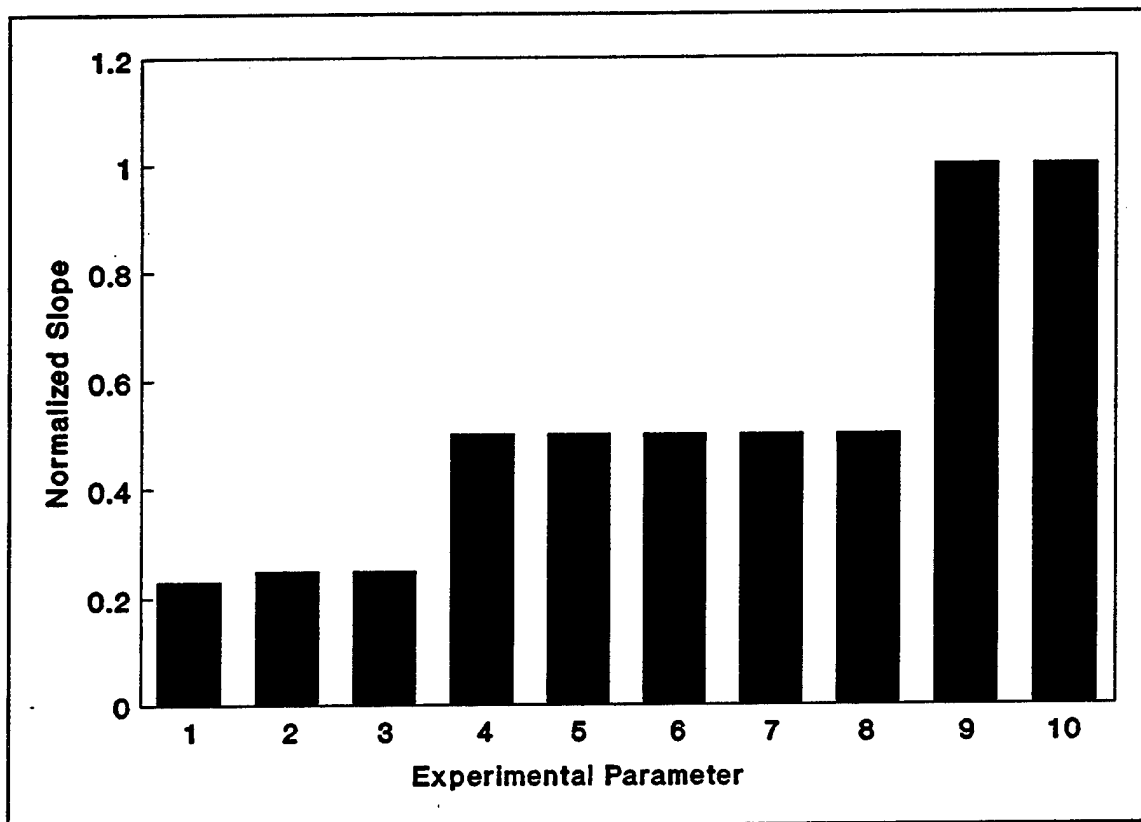


Fig. 1. Normalized average slopes of parameter sensitivity curves for  $\chi^{(3)}_{\text{solute}}$ .

Parameters shown in Fig. 1:

- |                                 |                                |
|---------------------------------|--------------------------------|
| 1 -- Sample absorption          | 6 -- CS <sub>2</sub> thickness |
| 2 -- $I_{\text{solution}}$      | 7 -- Sample mass               |
| 3 -- $I_{\text{CS}_2}$          | 8 -- Sample volume             |
| 4 -- $\chi^{(3)}_{\text{CS}_2}$ | 9 -- $n_{\text{CS}_2}$         |
| 5 -- Sample thickness           | 10 -- $n_{\text{solution}}$    |

Figure 2 shows that  $\langle \gamma \rangle$  is also most sensitive to uncertainty in the refractive indices of CS<sub>2</sub> and sample solution. The increased dependence on  $n_{\text{solution}}$  is due to its presence in the local field factor (Equation 3).

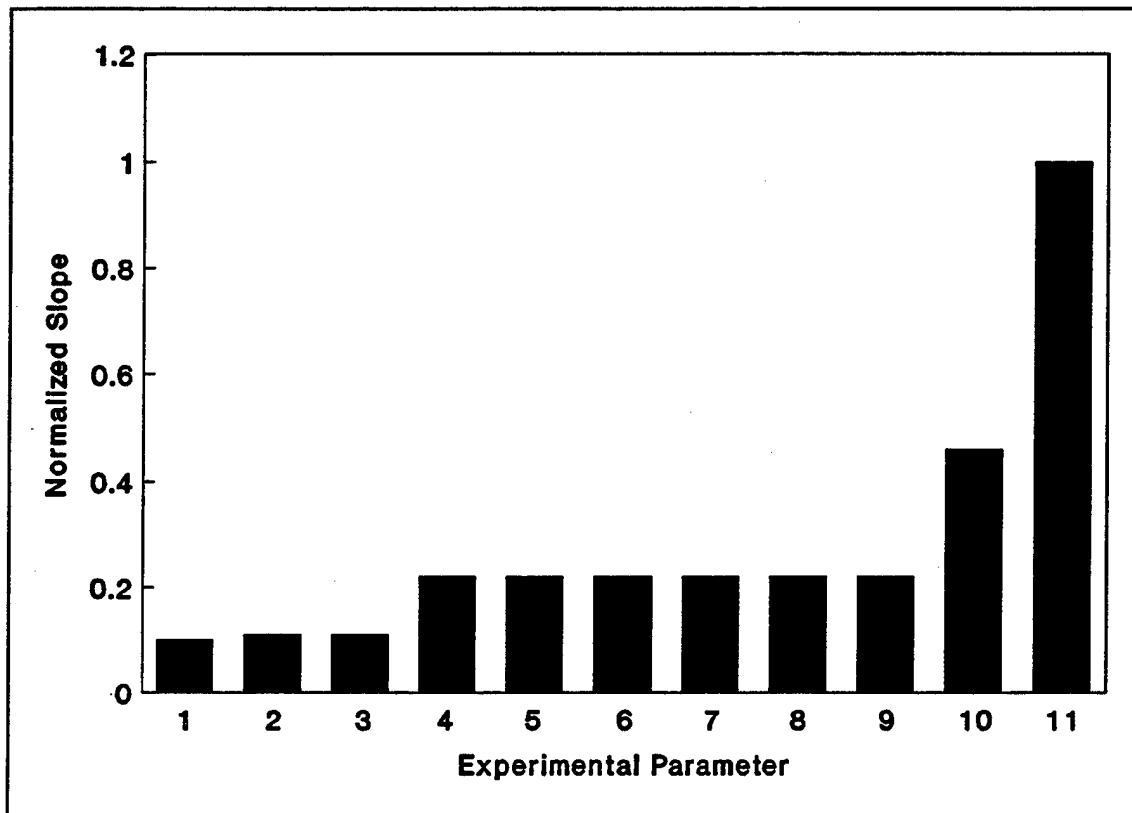


Fig. 2. Normalized average slopes of parameter sensitivity curves for  $\langle \gamma \rangle$ .

Parameters shown in Fig. 2:

- |                                 |                             |
|---------------------------------|-----------------------------|
| 1 -- Sample absorption          | 7 -- Molecular weight       |
| 2 -- $I_{\text{solution}}$      | 8 -- Sample mass            |
| 3 -- $I_{\text{CS}_2}$          | 9 -- Sample volume          |
| 4 -- $\chi_{\text{CS}_2}^{(3)}$ | 10 -- $n_{\text{CS}_2}$     |
| 5 -- Sample thickness           | 11 -- $n_{\text{solution}}$ |
| 6 -- $\text{CS}_2$ thickness    |                             |

## RESULTS

A sampling of eight compounds evaluated for  $\chi^{(3)}$  and  $\langle \gamma \rangle$  reveals average  $\chi^{(3)}$  and  $\langle \gamma \rangle$  uncertainties of 8% and 9%, respectively, with values ranging from 6% to 10% for  $\chi^{(3)}$  and 6% to 12% for  $\langle \gamma \rangle$ . In general, the lowest percent error is attributable to the highest voltage signal. Higher  $\chi^{(3)}$  and  $\langle \gamma \rangle$  values have higher associated phase-conjugate voltage readings and, therefore, lower percent uncertainties. For example, a material with a  $\chi^{(3)}$  in the area of  $10^{-9}$  will have a percent uncertainty of about 7% whereas a  $\chi^{(3)}$  of  $10^{-13}$  can have an uncertainty as high as 40%.

Table 4 shows the results obtained for zinc tetraphenyl tetrabenzporphyrin in tetrahydrofuran. It can be seen from these data that while the absolute uncertainty varies with concentration, the percent uncertainty remains relatively constant.

Table 4. Experimental results for zinc tetraphenyl tetrabenzporphyrin in tetrahydrofuran.

C (g/mL)	$\chi^{(3)}$ solution ( $\times 10^{-13}$ esu)	$\chi^{(3)}$ solute ( $\times 10^{-10}$ esu)	$\langle \gamma \rangle$ ( $\times 10^{-31}$ esu)
0.00216	43.7 ±1.78 (4%)	20.1 ±0.82 (4%)	6.66 ±0.38 (6%)
0.00076	14.5 ±0.59 (4%)	18.8 ±0.78 (4%)	6.26 ±0.36 (6%)
0.00038	9.57 ±0.39 (4%)	24.5 ±1.04 (4%)	8.12 ±0.48 (6%)
0.00019	6.34 ±0.25 (4%)	32.1 ±1.44 (4%)	10.6 ±0.64 (6%)
0.00010	2.31 ±0.09 (4%)	21.2 ±1.14 (5%)	7.03 ±0.48 (7%)
0	0.24 ±0.01 (4%)	-- --	-- --

Figure 3 shows the curve fit data from Table 4 where  $\chi^{(3)}$ <sub>solute</sub> versus concentration is shown. The straight line is obtained by plotting Eq. 24 with  $\chi^{(3)}$ <sub>solvent</sub> =  $2.4 \times 10^{-14}$  esu,  $\chi^{(3)}$ <sub>solute</sub> =  $2.0 \times 10^{-9}$  esu, and the concentrations shown in Table 4. Specific values for  $\chi^{(3)}$ <sub>solute</sub> are compared in Table 5 to experimental values obtained from Table 4. Percent errors given in Table 5 are calculated with the assumption that the curve-fit values are the more correct. It is generally expected that experimental deviations from the curve-fit line will be within one or two standard deviations as given in Table 4, or at most about 10%. Absolute errors shown in Table 5, in two cases, are outside predicted uncertainty. It is currently believed that these relatively large percent errors are due to fluctuations in laser power; a variable which has not been considered in the uncertainty analysis. Variations, however, appear to be random and are expected to average out in the curve fitting process.

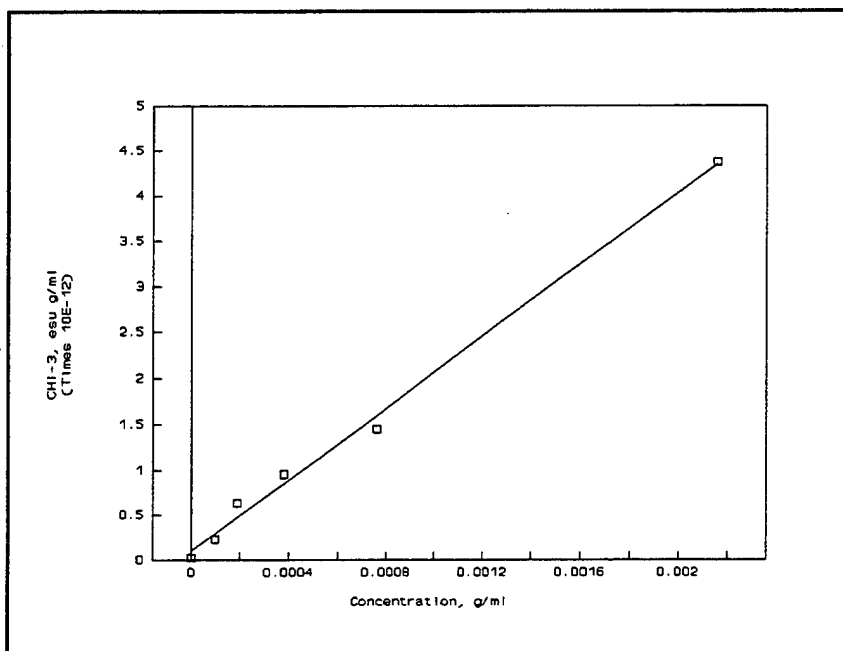


Fig. 3. Experimental data and curve-fit line versus concentration for zinc tetraphenyl tetrabenzporphyrin in tetrahydrofuran.

Table 5. Comparison of experimental and curve-fit data for zinc tetraphenyl tetrabenzporphyrin in tetrahydrofuran.

C (g/mL)	Experimental $\chi^{(3)}$ <sub>solution</sub> ( $\times 10^{-13}$ esu)	Curve-Fit $\chi^{(3)}$ <sub>solution</sub> ( $\times 10^{-13}$ esu)	Percent Error
0.00216	43.7	43	2%
0.00076	14.5	15	4%
0.00038	9.57	7.8	23%
0.00019	6.34	4.0	57%
0.00010	2.31	2.2	5%
0	0.24	0.24	0%

## CONCLUSIONS AND RECOMMENDATIONS

Uncertainty expressions have been derived and used to evaluate a DFWM scheme used in the determination of third-order susceptibility and molecular second hyperpolarizability of nonlinear optical materials.

The results of a representative experimental run are presented showing that, for samples in solution, the greatest uncertainty is currently introduced by phase-conjugate voltage readings. As the strength of the phase-conjugate signal decreases, the overall experimental uncertainty increases. This relationship can occur as a result of a low laser output intensity or by the nonlinear material having a low phase-conjugate signal strength. Maximum experimental accuracy can be assured with proper laser maintenance and system alignment to optimize laser energy output and phase-conjugate signal strength.

Parameter sensitivity curves reveal that the indices of refraction of both the sample in solution and reference solution are the most critical parameters with respect to overall experimental uncertainty. Solution refractive indices are currently assumed equal to those of the solution solvent; the validity of this assumption should be verified in light of the results of this study.

Sensitivity plots contained in this report can be used as a general guide in estimating the impact of changes in tolerances of experimental variables. Accompanying software is now routinely used in DFWM experiments in determining  $\chi^{(3)}$  and  $\langle \gamma \rangle$  and their associated uncertainties.

Actual experimental deviations from a least-squares curve were shown to be within predicted uncertainties with the exception of some outliers attributable to variation in laser output power, which was not considered in the analysis.

Concerning the investigation of trends: results show that changes of  $\pm 10\%$  percent or greater in  $\chi^{(3)}$  and  $\langle \gamma \rangle$  can be considered statistically significant. This confidence interval can be decreased by increasing the number of points (concentrations) used in the least-squares approximation.

The method of determining solution concentration outlined here has proven to be of acceptable accuracy ( $\pm 1.6\%$ ) while also minimizing the production of hazardous waste and the time required to complete an experimental run.

It is believed that this study has given significant insight into the experimental uncertainties inherent to the DFWM technique when used in the evaluation of third-order susceptibility and molecular second hyperpolarizability of nonlinear optical materials.

#### REFERENCES

1. Rao, D.V.G.L.N., Aranda, F.J., Roach, J.F., Remy, D.E., *Appl. Phys. Lett.*, 1991, 58, 1241-1243.

## APPENDICES

- A. Derivation of Mass/Concentration Expression
- B. Computer Program ERRCHI-3.BAS
- C. Parameter Sensitivity Curves

## APPENDIX A. Derivation of Mass/Concentration Expression

A technique has been developed to determine dilute solution concentrations from accurate weight measurements. The derivation is as follows:

An initial predetermined concentration  $C_i$  is prepared of weight  $m_i$  and density  $\rho$ . Some solution is removed for measurement and the sample is weighed again. This final weight is  $m_f$ . To determine the final volume  $V_f$  we can write:

$$V_f = \frac{m_f}{\rho}. \quad (\text{A1})$$

The mass of the solute contained in  $V_f$  can be determined by the expression

$$m_{\text{solute}} = C_i V_f. \quad (\text{A2})$$

Some solvent is added to dilute the solution for the next measurement. This new, added volume can be obtained by the expression

$$V_n = \frac{m_n - m_f}{\rho}. \quad (\text{A3})$$

The new concentration is

$$C_n = \frac{m_{\text{solute}}}{V_f + V_n}. \quad (\text{A4})$$

Inserting Eqs. A1, A2 and A3 into Eq. A4, we obtain the expression

$$C_n = \frac{C_i \frac{m_f}{\rho}}{\frac{m_f}{\rho} + \frac{m_n - m_f}{\rho}}, \quad (\text{A5})$$

which reduces to

$$C_n = C_i \frac{m_f}{m_n}. \quad (\text{A5})$$

APPENDIX B. Program ERRCHI-3.BAS

```

10  REM This program calculates CHI-3 and Gamma for samples in solution.
20  REM It can be used in conjunction with Lotus spreadsheet CHI-3.WK1
30  REM which uses a least-squares curve-fitting routine to determine
40  REM solute CHI-3 values from solution CHI-3 values calculated
50  REM with this program.  B. Kimball, 18 March 1994.
60
70  CLS
100 INPUT "I of solution (mv) = ", Isol
110 INPUT "I of CS2, (mv) = ", Ics
120 REM Ics = 50000
130 INPUT "Absorbance, = ", ab
140 INPUT "Concentration, (mg/ml) = ", con
143
144 REM          PARAMETERS FOR CHI-3 AND GAMMA EVALUATION

145 REM Index of refraction of solution
147 ns = 1.44
150 REM Path Length CS-2, (mm)
155 DCS = 2
160 REM Path length solution, (mm)
162 DS = 2
165 REM CHI-3 of Solvent, (esu)
167 Xsolv = 2.4E-14
168 REM Uncertainty in Solvent CHI-3
170 WXsolv = 9.7E-16
172 REM CHI-3 of CS-2
174 XCS = 6.8E-13
175 REM Index of refraction of CS-2
180 ncs = 1.63
182 REM Molecular weight of solute, g/mole
184 M = 678
186 REM Avogadros number
188 A = 6.023E+23
190 REM Mass of sample (mg)
195 mg = 3.8
200 REM Volume of Solvent used in solution
205 ml = 5

210 REM          PARAMETERS FOR CHI-3 UNCERTAINTY

220 PWXCS = 0
230 WXcs = XCS * PWXCS
240 PWisol = .05
250 Wisol = Isol * PWisol
260 PWics = .05
270 Wics = Ics * PWics
280 PWns = .01
290 Wns = ns * PWns
300 PWncs = .001
310 Wncs = ncs * PWncs
320 PWDS = .001
330 WDS = DS * PWDS
340 PWDCS = .001
350 WDCS = DCS * PWDCS
360 PWab = .0008
370 Wab = ab * PWab
380 PWM = .001
390 WM = M * PWM
392 PWmg = .01

```

```

394 Wmg = mg * PWmg
396 PWml = .01
398 Wml = ml * PWml

```

```

400 REM          CALCULATE CHI-3 AND GAMMA

```

```

405 alpha = -LOG(10 ^ -ab)
410 P1 = Isol / Ics
420 P2 = ns / ncs
430 P3 = DCS / DS
440 P4 = (alpha / (1 - (EXP(-alpha)))) * EXP(alpha / 2)
450 Xsol = XCS * (P1 ^ .5) * (P2 ^ 2) * P3 * P4
460 Xsam = (Xsol - Xsolv) / (con / 1000)
470 L = (ns ^ 2 + 2) / 3
480 GAMMA = (Xsam * M) / (L ^ 4 * A)

```

```

490 REM          CALCULATE Xsol UNCERTAINTY

```

```

495 REM  Sensitivity Expressions
500 SXcs = (P1 ^ .5) * (P2 ^ 2) * P3 * P4
510 SIsol = XCS * .5 * ((Isol ^ .5) ^ -1) * ((Ics ^ .5) ^ -1) *
      P2 ^ 2 * P3 * P4
520 Sics = XCS * .5 * ((Isol ^ .5) / (Ics ^ 1.5)) * P2 ^ 2 * P3 * P4
530 Sns = XCS * (P1 ^ .5) * 2 * ns / (ncs ^ 2) * P3 * P4
540 Sncs = XCS * (P1 ^ .5) * 2 * (2 / (ncs ^ 3)) * P3 * P4
550 SDCS = XCS * (P1 ^ .5) * (P2 ^ 2) * (1 / DS) * P4
560 SDS = XCS * (P1 ^ .5) * (P2 ^ 2) * (DCS / (DS ^ 2)) * P4
570 Sab = XCS * (P1 ^ .5) * P2 ^ 2 * P3 * ((1 - EXP(-alpha)) * ((alpha / 2) +
      EXP(alpha / 2)) - alpha * EXP(-alpha / 2)) / ((1 - EXP(-alpha)) ^ 2)

```

```

580 REM  Parameter Uncertainties

```

```

590 UXcs = SXcs * WXcs
600 UIsol = SIsol * WIsol
610 UIcs = Sics * WIcs
620 Uns = Sns * Wns
630 Uncs = Sncs * Wncs
640 UDCS = SDCS * WDCS
650 UDS = SDS * WDS
660 Uab = Sab * Wab

```

```

670 REM Xsol Uncertainty

```

```

680 WXsol = (UXcs ^ 2 + UIsol ^ 2 + UIcs ^ 2 + Uns ^ 2 + Uncs ^ 2 +
      UDCS ^ 2 + UDS ^ 2 + Uab ^ 2) ^ .5

```

```

700 REM          CALCULATE con UNCERTAINTY

```

```

710 REM  Sensitivity Expressions

```

```

720 Smg = 1 / ml
730 Sml = mg / (ml ^ 2)

```

```

740 REM  Parameter Uncertainties

```

```

750 Umg = Smg * Wmg
760 Uml = Sml * Wml

```

```

770 REM  con Uncertainty

```

```

780 Wcon = (Umg ^ 2 + Uml ^ 2) ^ .5

```

```

800 REM          CALCULATE Xsam UNCERTAINTIES

810 REM Sensitivity Expressions
820 SXsol = 1000 / con
830 SXsolv = 1000 / con
840 Scon = 1000 * (Xsol - Xsolv) / (con ^ 2)

850 REM Parameter Uncertainties
860 UXsol = SXsol * WXsol
870 UXsolv = SXsolv * WXsolv
880 Ucon = Scon * Wcon

890 REM Xsam Uncertainty
900 WXsam = (UXsol ^ 2 + UXsolv ^ 2 + Ucon ^ 2) ^ .5

950 REM          CALCULATE L UNCERTAINTIES

960 REM Sensitivity Expressions
970 SLn = 2 * ns / 3

980 REM Parameter Uncertainties
990 ULn = SLn * Wns

1000 REM L Uncertainty
1010 WL = ULn

1020 REM          CALCULATE GAMMA UNCERTAINTIES

1030 REM Sensitivity Expressions
1040 SXsam = M / ((L ^ 4) * A)
1050 SM = Xsam / ((L ^ 4) * A)
1060 SL = 4 * Xsam * M / ((L ^ 5) * A)

1070 REM Parameter Uncertainties
1080 UXsam = SXsam * WXsam
1090 UM = SM * WM
1100 UL = SL * WL

1110 REM GAMMA Uncertainty
1120 WGAMMA = (UXsam ^ 2 + UM ^ 2 + UL ^ 2) ^ .5

1200 REM          PRINT RESULTS

1204 PRINT "          RESULTS"
1205 PRINT
1210 PRINT "CHI-3 of solution is"; Xsol
1220 PRINT "Uncertainty"; WXsol
1230 PRINT
1240 PRINT "CHI-3 of sample is"; Xsam
1250 PRINT "Uncertainty"; WXsam
1260 PRINT
1270 PRINT "Gamma of the solute is"; GAMMA
1280 PRINT "Uncertainty"; WGAMMA

```

```

1310 PRINT "          PARAMETER UNCERTAINTIES"
1320 PRINT
1330 PRINT "          Xsol"
1340 PRINT "CHI-3 of CS2 "; UXcs
1350 PRINT "Voltage reading for solution"; UIsol
1360 PRINT "Voltage reading for CS2"; UIcs
1370 PRINT "Solution refractive index"; Uns
1380 PRINT "CS2 refractive index"; Uncs
1390 PRINT "Solution thickness"; UDS
1400 PRINT "CS2 thickness"; UDCS
1410 PRINT "Absorption"; Uab
1415 INPUT ; "Hit Return", me
1416 CLS
1420 PRINT
1430 PRINT "          Concentration"
1440 PRINT "Weight"; Umg
1450 PRINT "Volume"; Uml
1470 PRINT
1480 PRINT "          Xsam"
1490 PRINT "Solution CHI-3"; UXsol
1500 PRINT "Solvent CHI-3"; UXsolv
1510 PRINT "Concentration"; Ucon
1520 PRINT
1530 PRINT "          Field Factor L"
1540 PRINT "Solution refractive index"; ULn
1550 PRINT
1560 PRINT "          GAMMA"
1570 PRINT "Sample CHI-3"; UXsam
1580 PRINT "Molecular weight"; UM
1590 PRINT "Field Factor L"; UL
1700 END

```

APPENDIX C. Parameter Sensitivity Curves.

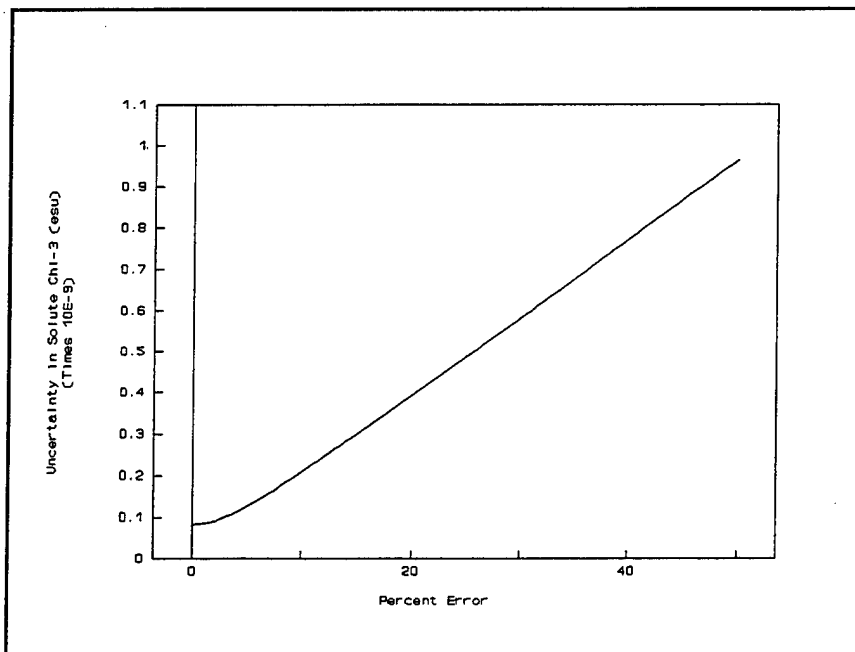


Fig. C1. Uncertainty in  $\chi^{(3)}$  resulting from percent error in the assumed value for the  $\chi^{(3)}$  of  $\text{CS}_2$ .

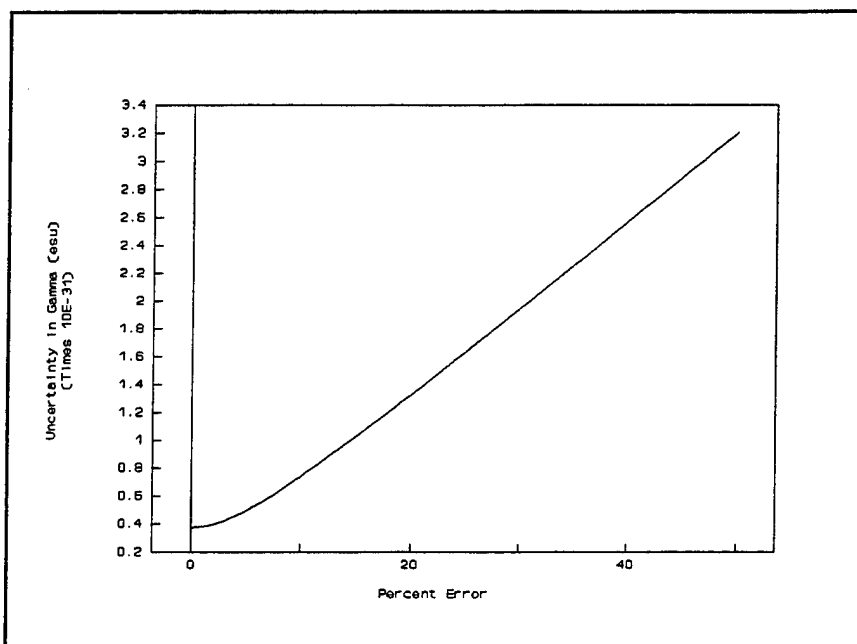


Fig. C2. Uncertainty in  $\langle \gamma \rangle$  resulting from percent error in the assumed value for the  $\chi^{(3)}$  of  $\text{CS}_2$ .

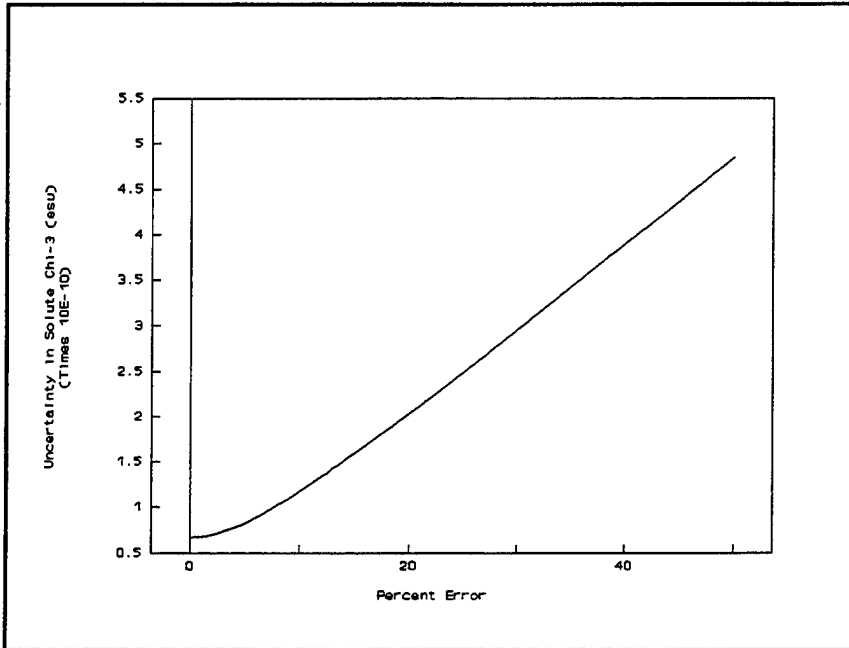


Fig. C3. Uncertainty in  $\chi^{(3)}$  solute resulting from percent error in the DFWM phase-conjugate signal of the solution.

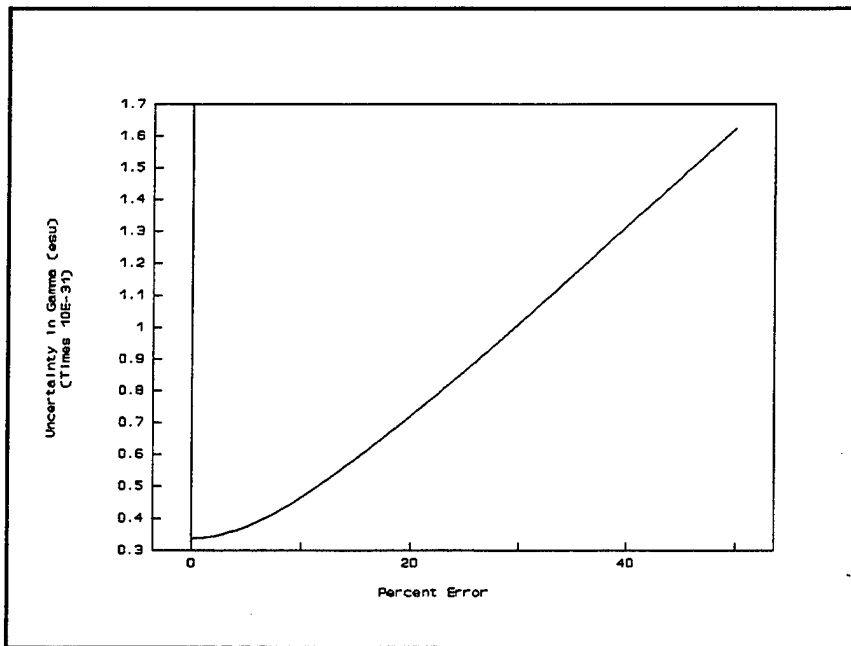


Fig. C4. Uncertainty in  $\langle \gamma \rangle$  resulting from percent error in the DFWM phase-conjugate signal of the solution.

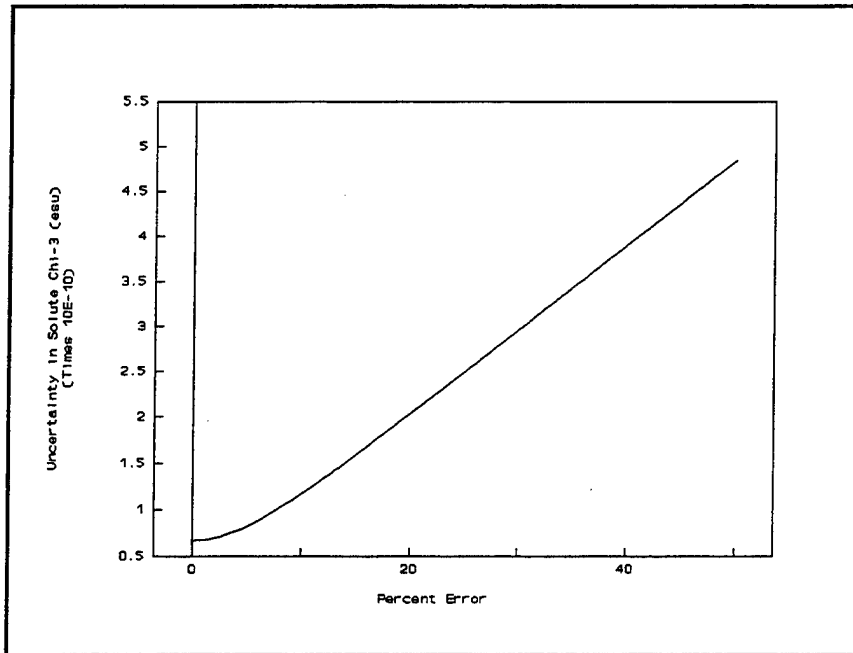


Fig. C5. Uncertainty in  $\chi^{(3)}$  solute resulting from percent error in the DFWM phase-conjugate signal of  $\text{CS}_2$ .

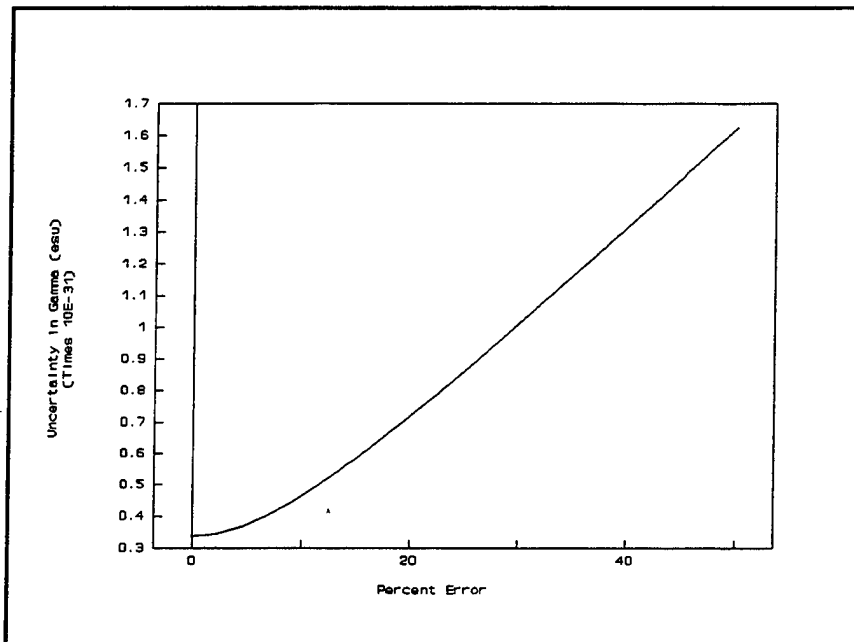


Fig. C6. Uncertainty in  $\langle \gamma \rangle$  resulting from percent error in the DFWM phase-conjugate signal of  $\text{CS}_2$ .

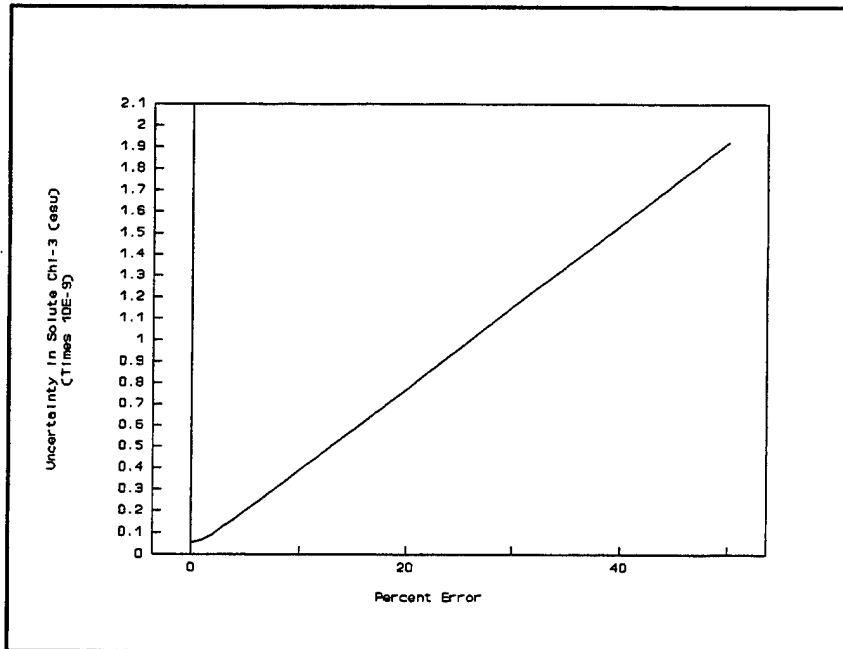


Fig. C7. Uncertainty in  $\chi^{(3)}$  solute resulting from percent error in the index of refraction of the solution.

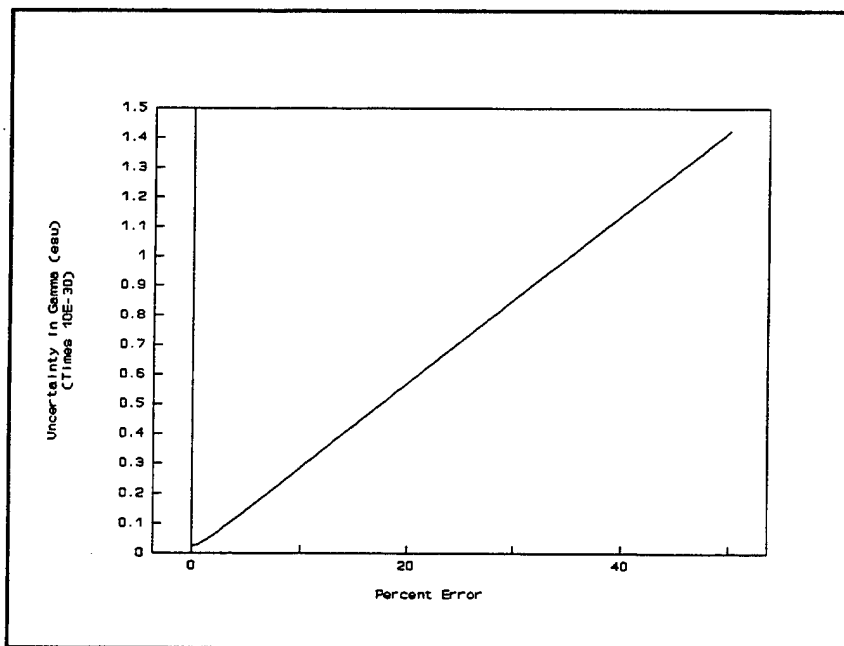


Fig. C8. Uncertainty in  $\langle \gamma \rangle$  resulting from percent error in the index of refraction of the solution.

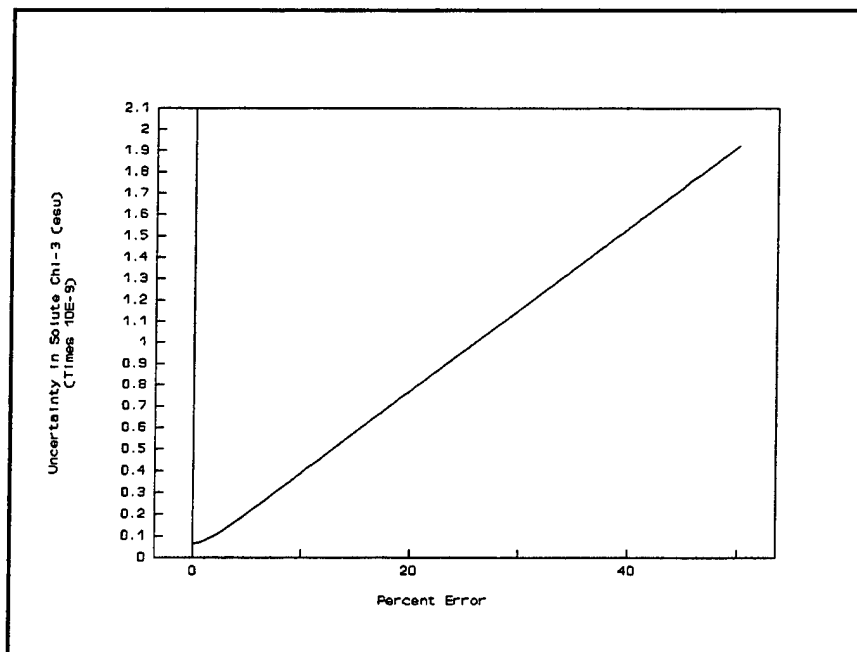


Fig. C9. Uncertainty in  $\chi^{(3)}$  solute resulting from percent error in the index of refraction of  $\text{CS}_2$ .

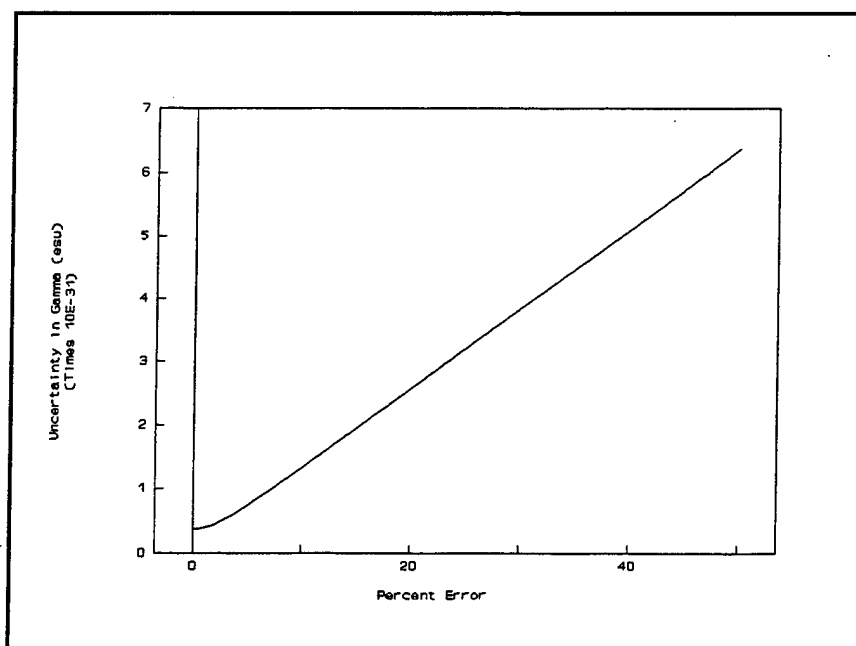


Fig. C10. Uncertainty in  $\langle \gamma \rangle$  resulting from percent error in the index of refraction of  $\text{CS}_2$ .

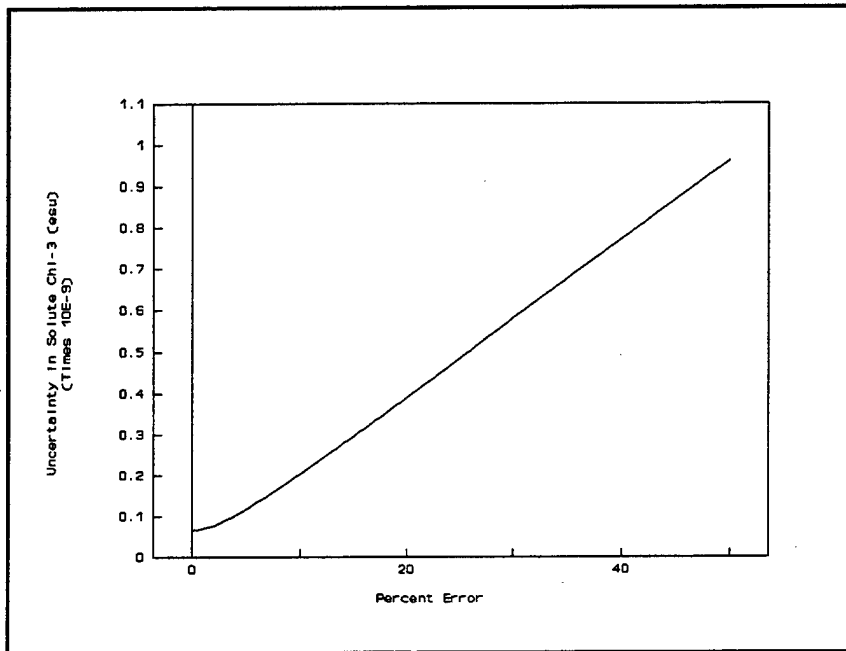


Fig. C11. Uncertainty in  $\chi^{(3)}$  solute resulting from percent error in sample thickness.

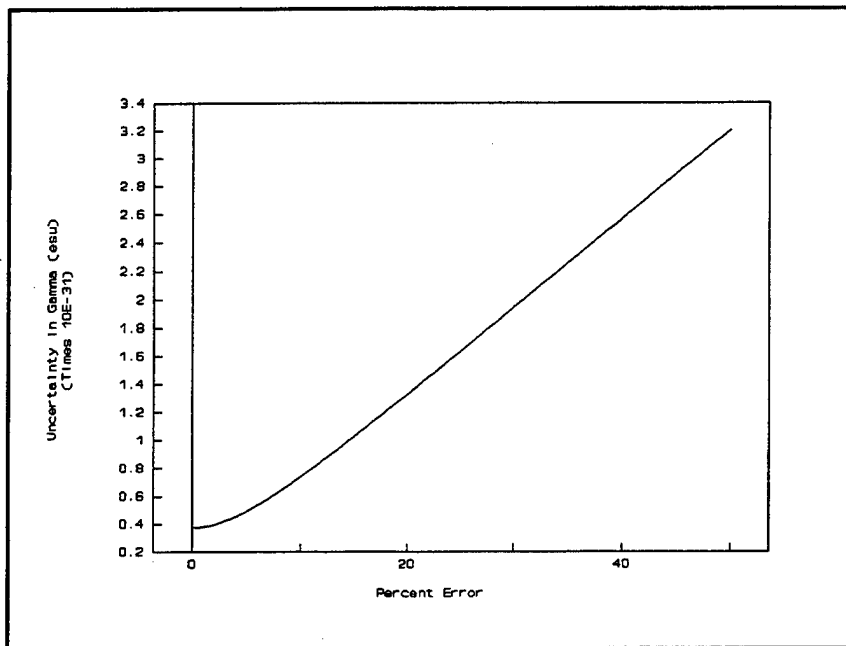


Fig. C12. Uncertainty in  $\langle \gamma \rangle$  resulting from percent error in sample thickness.

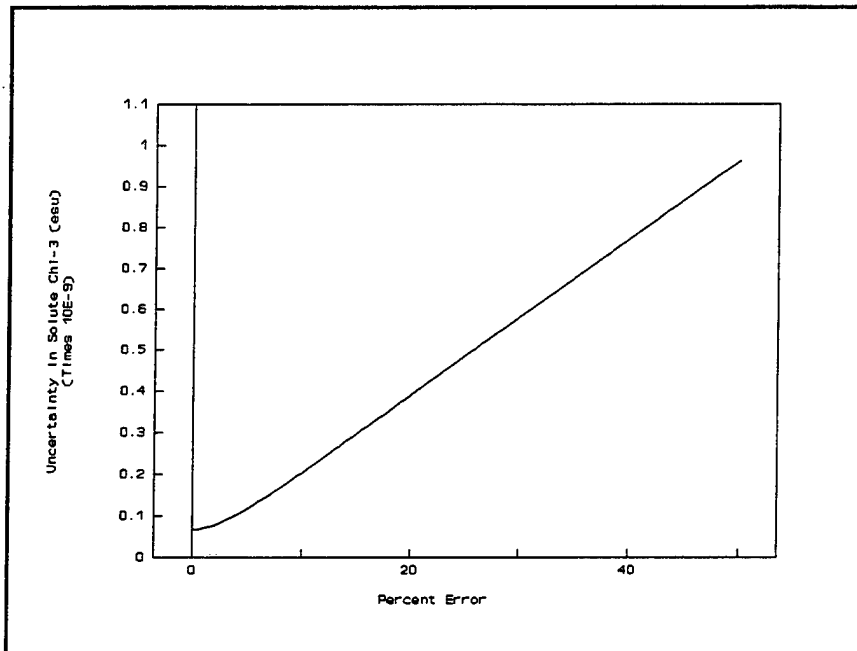


Fig. C13. Uncertainty in  $\chi^{(3)}$  solute resulting from percent error in  $\text{CS}_2$  thickness.

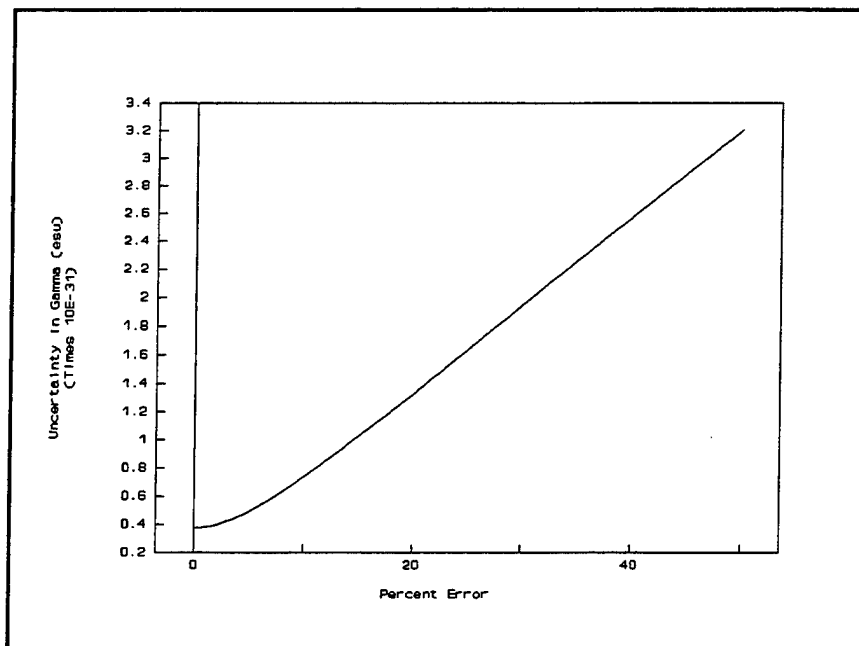


Fig. C14. Uncertainty in  $\langle \gamma \rangle$  resulting from percent error in  $\text{CS}_2$  thickness.

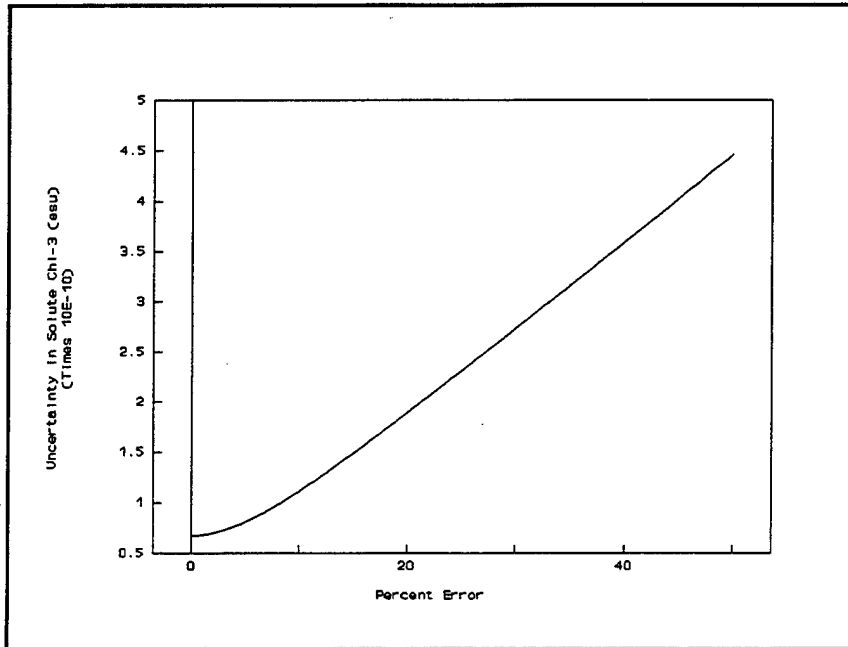


Fig. C15. Uncertainty in  $\chi^{(3)}$  solute resulting from percent error in sample absorption.

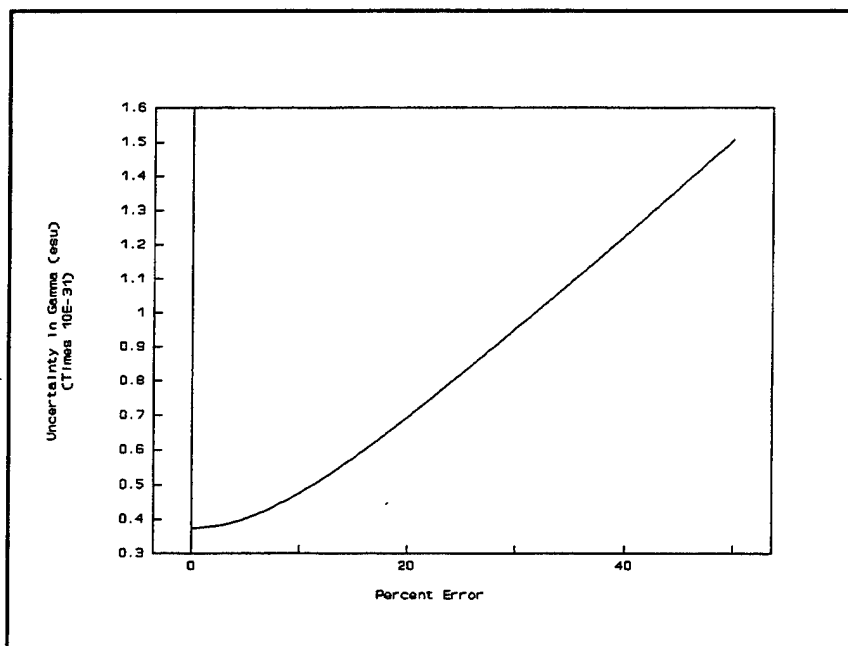


Fig. C16. Uncertainty in  $\langle \gamma \rangle$  resulting from percent error in sample absorption.

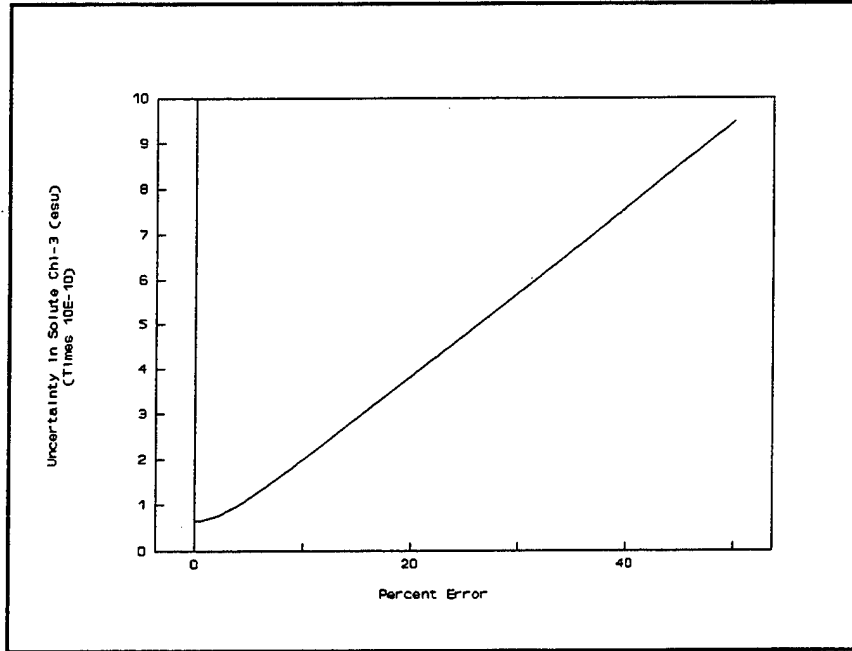


Fig. C17. Uncertainty in  $\chi^{(3)}$  solute resulting from percent error in measurement of solution weight.

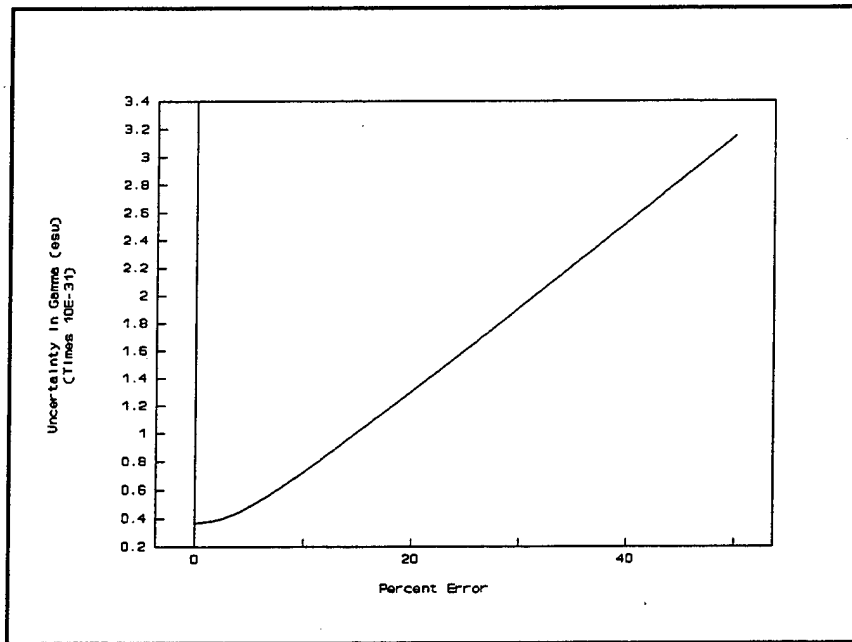


Fig. C18. Uncertainty in  $\langle \gamma \rangle$  resulting from percent error in measurement of solution weight.

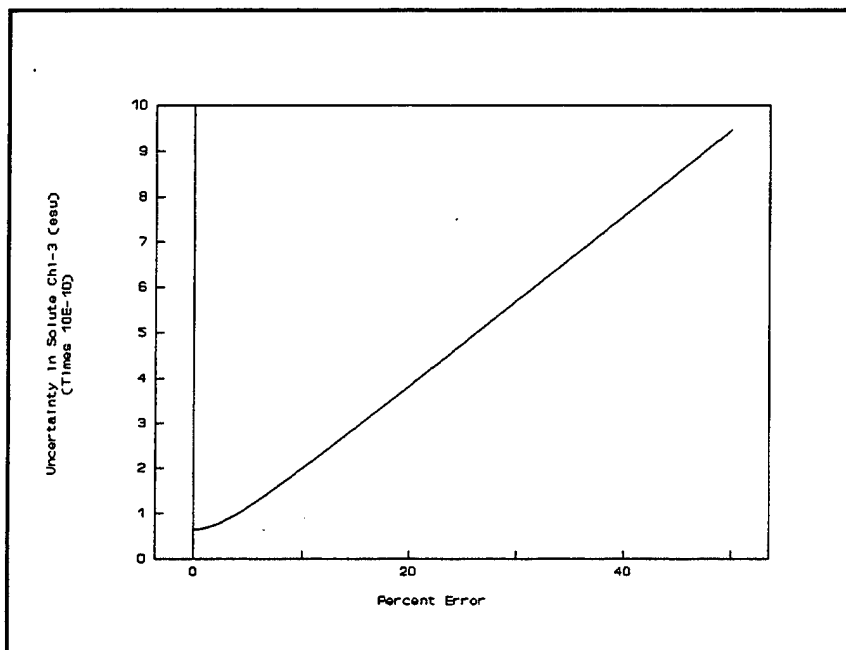


Fig. C19. Uncertainty in  $\chi^{(3)}$  solute resulting from percent error in measurement of solution volume.

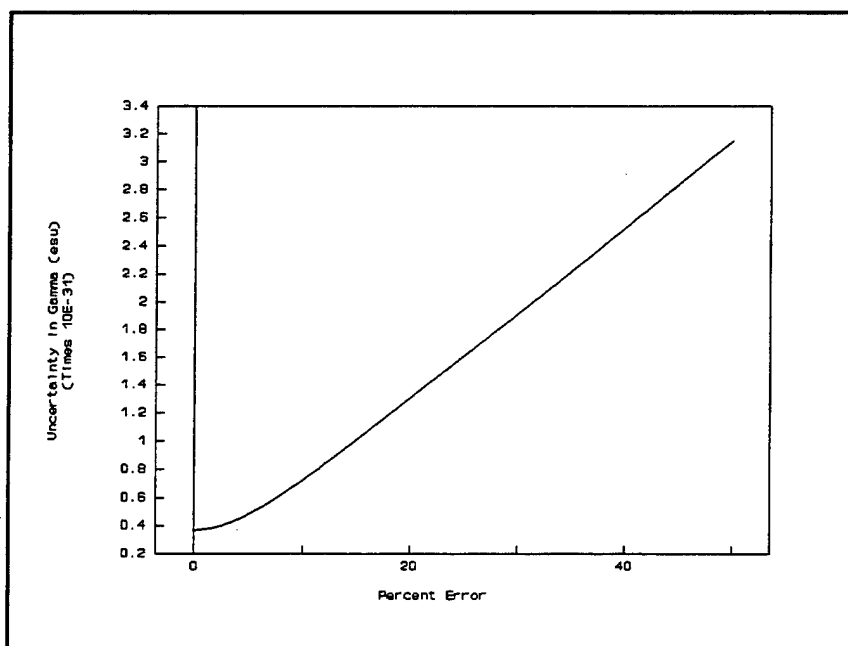


Fig. C20. Uncertainty in  $\langle \gamma \rangle$  resulting from percent error in measurement of solution volume.

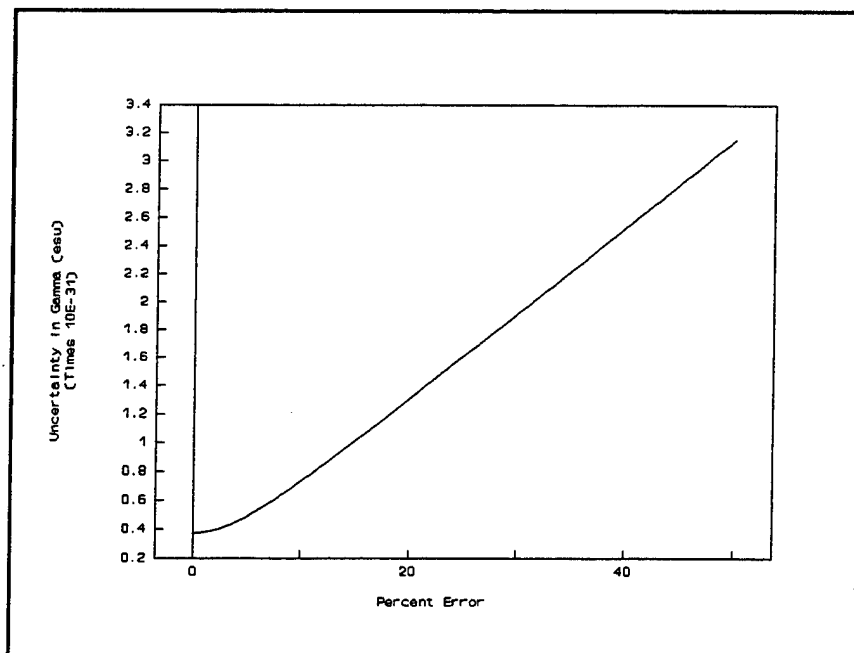


Fig. C21. Uncertainty in  $\langle \gamma \rangle$  resulting from percent error in molecular weight of solute.

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