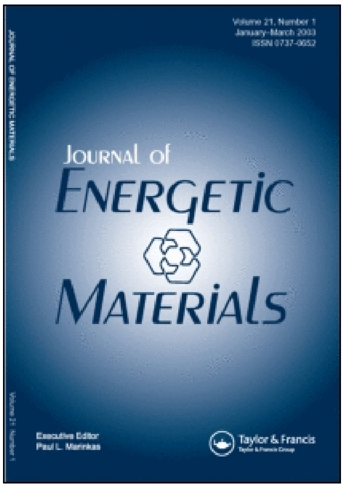

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PLASTICIZER MIGRATION IN NITROCELLULOSE-BASED PROPELLANTS

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ABSTRACT

An "environmentally-friendly" technique for determining plasticizer concentration profiles in propellant sheets has been developed. The method was developed in response to a need for a quick, accurate means to study plasticizer migration in experimental gun propellants. Evidence of rapid migration between laminated sheets of nitrocellulose-based propellant containing different amounts of two nitrate ester plasticizers was obtained. An estimate of the diffusion coefficients for one of these plasticizers was also obtained.

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INTRODUCTION

Traditional gas and liquid chromatographic techniques for the analysis of plasticizer content in solid propellants depend on the use of organic solvents, many pieces of glassware, and in most cases, significant amounts of time for extraction and standardization. Use of any of these techniques for the determination of high resolution plasticizer profiles across a thin sheet of propellant can be very difficult, and will most certainly result in the generation of relatively large quantities of reactive waste from extraction solutions, wash solutions from the cleaning of glassware, and usually, waste solvent if a liquid chromatographic technique is used. In addition, relatively large quantities of sample are usually required. For experimental formulations, this is not always practical. The technique developed for this investigation successfully meets the need for a quick, reliable method, and does so without the generation of hazardous waste and the consumption of large amounts of the experimental propellants.

The samples studied were layered, nitrocellulose-based solid propellants. The concern of the propellant formulators was that migration of plasticizer would occur between layers in the laminated propellant, and that the result would be a homogeneous propellant, rather than one with distinct layers. The challenge was to examine the aging characteristics of the propellants by obtaining individual plasticizer concentration profiles in a layered propellant whose total thickness was on the order of only

2-4 mm. This was accomplished by means of desorption-GC-MS, an environmentally friendly technique which requires no solvents, and therefore generates very little waste. Using this technique, quantitative profiles of plasticizer content were obtained for an experimental laminate propellant. Comparison of experimental results with predicted concentration profiles indicated that significant migration between the layers occurred in certain formulations. Additional experiments performed on layered propellants prepared in the laboratory provided data for estimation of diffusion coefficients for two nitrate ester plasticizers.

EXPERIMENTAL

Samples

The experimental samples analyzed were based on nitrocellulose, and were plasticized with two nitrate ester plasticizers which shall be referred to as Plasticizer-P1 and Plasticizer-P2. A layered propellant (Propellant-A/B) was prepared by the manufacturer by pressing individual layers of Propellant-A and Propellant-B together between hot rollers. Analyses were performed when the laminated propellant was less than six week old (i.e. less than 6 weeks had elapsed since the time the laminated propellant had been fabricated).

Individual layers of propellant (unlaminated Propellant-A and Propellant-B) were also used in this study; Table 1 summarizes the nomenclature and formulations for these materials.

TABLE 1

Formulation of Individual Propellant Layers

Layer Name	Plasticizer-P1 (wt-%)	Plasticizer-P2 (wt-%)
Propellant-A	25	15
Propellant-B	5	38

Instrumentation:

Plasticizer levels were determined by means of desorption - gas chromatography - mass spectroscopy, D-GC-MS (see Figure 1). Desorption was achieved via a CDS Model 122 Pyroprobe® (coil type) connected through a heated (175°C) interface chamber to the splitless injector of a Hewlett Packard GC-FTIR/MS system (Model 5890 GC, Model 5970 MSD, and Model 5965 IRDs with narrow band MCT detector). The GC Column used was a Quadrex capillary column (0.32 mm x 25m; 3·Hm OV-17 film). The injector temperature was 200°C; the Pyroprobe® interface temperature was 175°C. The GC oven temperature program was as follows: 50°C isothermal for 1 min; 50-250°C at 70°/min; 250°C isothermal for 4 min. The Pyroprobe® was programmed to give a 20-s desorption pulse at 175°C. Mass spectral peaks used to quantify plasticizer concentrations were from propellant fragments (i.e. m/z = 73 for Plasticizer-P1, and 58 for Plasticizer P-2), rather than parent ions. Integration of chromatographic peaks for these selected ions was performed using Hewlett Packard ChemStation software. Figure 2 shows typical total ion chromatograms (TIC) and selected ion chromatograms (SIC).

Sample preparation:

Propellant slabs were cut with a microtome to give cross-sectional slices with a thickness of 200 um. The ends of each slice were trimmed to yield a rectangular sample with a length of approximately 3 mm. The nominal width of each rectangle was 1.8 mm. The mass of each slice was measured and recorded. To determine plasticizer concentration profiles across the width of the propellant sample, lengthwise strips were cut from the rectangular slice, and subjected to D-GC-MS analysis. Strips were held within the coils of the Pyroprobe® by first placing them in a quartz tube containing a small plug of glass wool, and then inserting the entire tube within the coils.

To get an estimate of the diffusion rate in laminate propellants which had *not* been subjected to hot rollers, a crude laminated propellant was prepared in the lab by clamping a layer of Propellant-A to a layer of Propellant-B. The resultant "laminate" was stored at room temperature for 42 hours, and then analyzed as described above.

Calculation of theoretical diffusion coefficients:

Calculations were performed starting with Fick's Law and assuming appropriate boundary conditions.[1]

$$\frac{\delta C}{\delta t} = D \frac{\delta^2 C}{\delta x^2}$$

Where C is the concentration of the species, t is time, D is the diffusion coefficient, and x thickness. The following assumptions were made: a) the two layers are of finite thickness and have a known concentration, b) the diffusion coefficient is independent of concentration, c) evaporation is negligible, and d) both layers are initially homogeneous and defect free. Based on these assumptions, the following expression is obtained for the concentration of Plasticer-P2 (a similar expression could be generated for Plasticizer-P1):

$$C_2(x,t) = \frac{L_A\ C_{A,2} + L_{AB}\ C_{B,2}}{L_{AB}} +$$

$$\frac{2}{L_{AB}} \sum_{n=1}^{n\_1} \exp\left(\frac{-Dn^2\pi^2 t}{L_{AB}^2}\right) \cos\left(\frac{n\pi x}{L_{AB}}\right) \left(\frac{L_3(C_{A,2}-C_{B,2})\sin(n\pi L_2/L_3) + C_{B,2}L_3\ \sin(n\pi)}{n\pi}\right)$$

Where D is the diffusion coefficient, L_A, is the thickness of Propellant-A, L_B is the thickness of Propellant-B, L_{AB} is the total thickness of the laminate, $C_{A,2}$ is the concentration of Plasticizer-P2 in the Propellant-A layer, $C_{B,2}$ is the concentration of Plasticizer-P2 in the Propellant-B layer, x is the position in the thickness direction, t is time, and n_1 is the number of terms used in the sum. Comparison of plots of $C_2(x,t)$ for values of n_1 equal to 10, 11, and 100 indicate that for times greater than 200 s, 10 terms are sufficient to describe $C_2(x,t)$.

RESULTS AND DISCUSSION

Instrument Calibration:

Typical curves are presented in Figure 3. Calibration curves were constructed based on multiple analysis of neat Propellant-A and Propellant-B, and consisted of measurements for just these two "standards" and a blank run. Correlation coefficients for these curves always exceeded 0.999, indicating the reliability of choosing the m/z=58 and 73 peaks for plasticizer analysis. Slopes and intercepts of the calibration curve varied slightly from day to day, making it necessary to construct a new curve for each new analysis. The reason why additional "standard" samples were not analyzed, is that they did not exist. While mixtures of desired ingredients could be prepared in the lab, we could not be sure that identical matrix effects would be duplicated. Furthermore, it would be difficult to prepare the desired samples in the lab without the use of solvents, which could potentially complicate the analysis.

"Depth" of individual layers was calculated based on cumulative ratios of the mass of individual strips to the mass of the total rectangular sample.

Plasticizer Profiles:

Figures 4 gives an experimentally determined profile for a Propellant-A/B laminate. The line drawn at a distance of approximately 0.7 mm indicates the approximate position of the visible boundary between the two layers in the propellant. Figure 5 illustrates the expected profiles for the cases of initial (no migration) and equilibrium states for the laminate Propellant-A/B. If no migration between layers had occurred, one would expect to see a Plasticizer-P1 profile that was a step function with 25 wt-%

in the Propellant-A layer, and 5 wt-% in the Propellant-B layer. Similarly, the Plasticizer-B level should be 15 wt-% in the Propellant-A layer and 38 wt-% in the Propellant-B layer. If equilibrium had already been established, one would expect to see approximately 12.3 wt-% of Propellant-P1 and 29.6 wt-% of Propellant-P2 in both layers of the laminate. What is actually observed in Figure 4 is a nearly flat profile for both Plasticizer-P1 and Plasticizer-P2. Visual inspection of the data suggests an "average" value across both layers that falls in the range of 11-14 wt% for Plasticizer-P2, and in the range of 24-29 wt-% for Plasticizer-P2. Based on an examination of this data, it is concluded that the system is near, or at, equilibrium, and that significant migration has occurred. For the sake of brevity, only one example of experimentally determined plasticizer profiles is presented in this paper. Numerous analyses have been performed; each yielded similar results and indicated the reproducibility of the technique.

Comparison with Theoretical Predictions:

Figure 6 gives calculated concentration profiles for three assumed diffusion coefficients. Based on a knowledge of "typical" values for diffusion coefficient, the time to reach a certain level of migration was calculated.[2,3] It was assumed that a slow migration process would have a diffusion coefficient on the order of 10^{-12} cm^2/s. The time necessary to reach equilibrium (i.e. the condition when the difference between the maximum and minimum concentration in the profile is less than or equal to 0.01%) was calculated to be nearly 800 years. For a system with a fast migration process, a diffusion coefficient of 10^{-10} was assumed. The calculated time-to-equilibrium in this case was nearly 8 years.

Considering the calculated concentration profiles and times-to-equilibrium, it was expected that the laminated Propellant-A/B should not experience a migration problem within the relatively short time-frame of this investigation. However, based on experimental results, it was concluded that migration occurs very rapidly, and that migration is therefore a very serious problem. Clearly, we had either been mistaken about "typical" values for diffusion coefficients, or had underestimated the effect of the thermal treatment to which the propellant layers had been subjected during processing. As the following discussion will explain, both factors contributed to the short equilibration time.

Estimation of Diffusion Coefficients

An estimation of the diffusion coefficient for Plasticizer-P1 and Plasticizer-P2 was obtained by analysis of a "laminated" Propellant-A/B which prepared in the lab. No solvent or thermal treatment was used to hold the layers together; they were simply clamped together and then stored at room temperature for 42 hours. By preparing the sample in this manner, it was expected that experimental artifacts would be minimized, and that a reasonable estimation of the diffusion coefficient would be obtained. Fits of the observed plasticizer profiles to the concentration equation described earlier were performed and the values for the diffusion coefficient of each plasticizer was obtained. Unfortunately, the error for the Plasticizer-P2 data was larger than the value of the diffusion coefficient itself, rendering it useless. Figure 7 (bottom) gives the data and fit for this determination. The value for the diffusion coefficient for Plasticizer-P1 was calculated to be on the order of 10^{-8} cm^2/s, and is considered to be reliable. Figure 7 (top) giveg the data and fit for this diffusion process. The calculated value for the diffusion coefficient for this ntrate ester plasticizer is 100 times faster than our previous "fast" estimate (i.e 10^{-10} cm^2/s), and suggests that migration occurs quite rapidly. An estimation of the time-to-equilibrium with a diffusion coefficient on the order of 10^{-8} cm^2/s is 0.08 years (approximately 28 days).

Literature values for the diffusion coefficient of nitroglycerine, a nitrate ester plasticizer, in several polyester resins also have magnitudes on the order of 10^{-8} cm^2/s. [4,5]

Discussions with the manufacturers of the laminated propellant revealed that during processing and curing, propellant is subjected to temperatures of approximately 70°C for a total of nearly 24 hours. At such a temperature, it is expected that the migration rate would be at least several times faster than at room temperature. This, together with the experimentally determined diffusion coefficient, provide ample explanation for the observed plasticizer profiles.

CONCLUSIONS

A new method for determination of plasticizer content in nitrocellulose-based propellants has been developed and applied to experimental laminated propellants. The method was developed such that it would be not only rapid and reliable, but that it would also provide concentration data with high spatial resolution.

Analysis of experimental propellants with the new method indicates that plasticizer migration is quite rapid and appears to be further encouraged by processing conditions.

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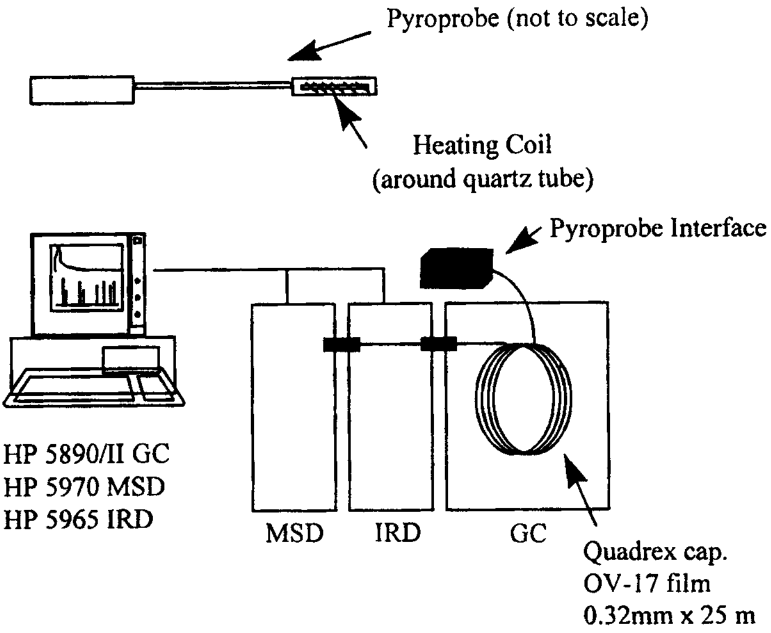


FIGURE 1

Experimental apparatus

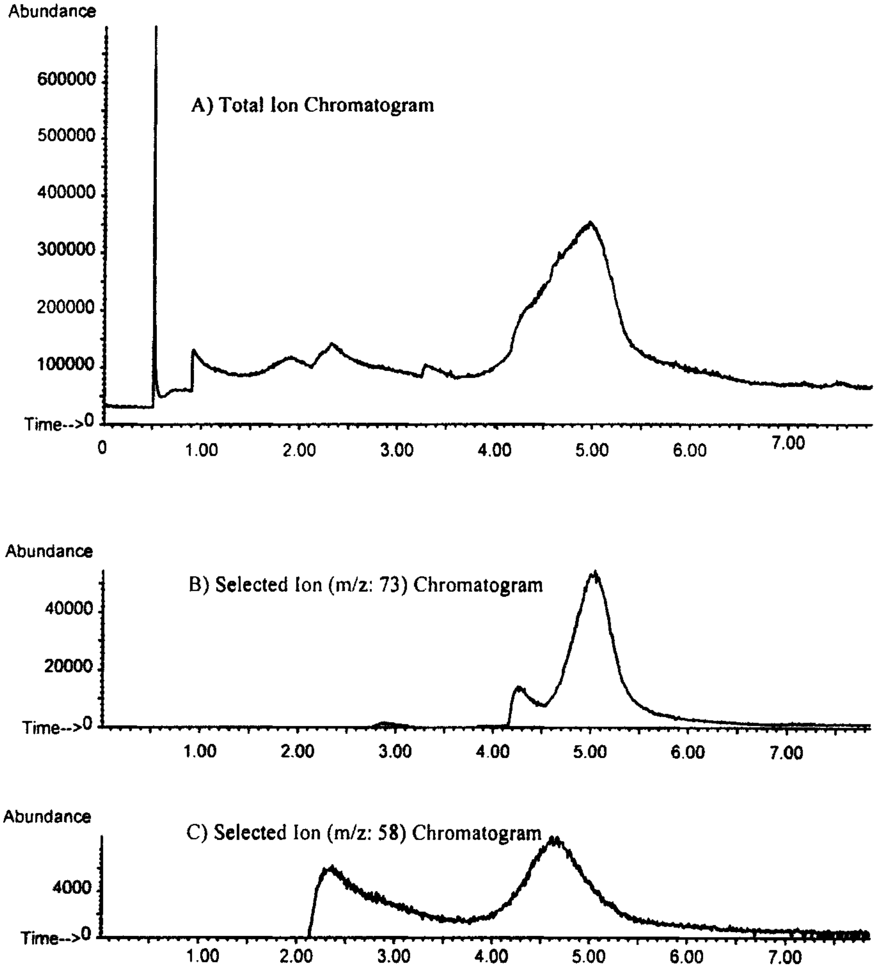


FIGURE 2

Total response chromatogram (TIC) and selected ion chromatogram (SIC) for Propellant-A/B

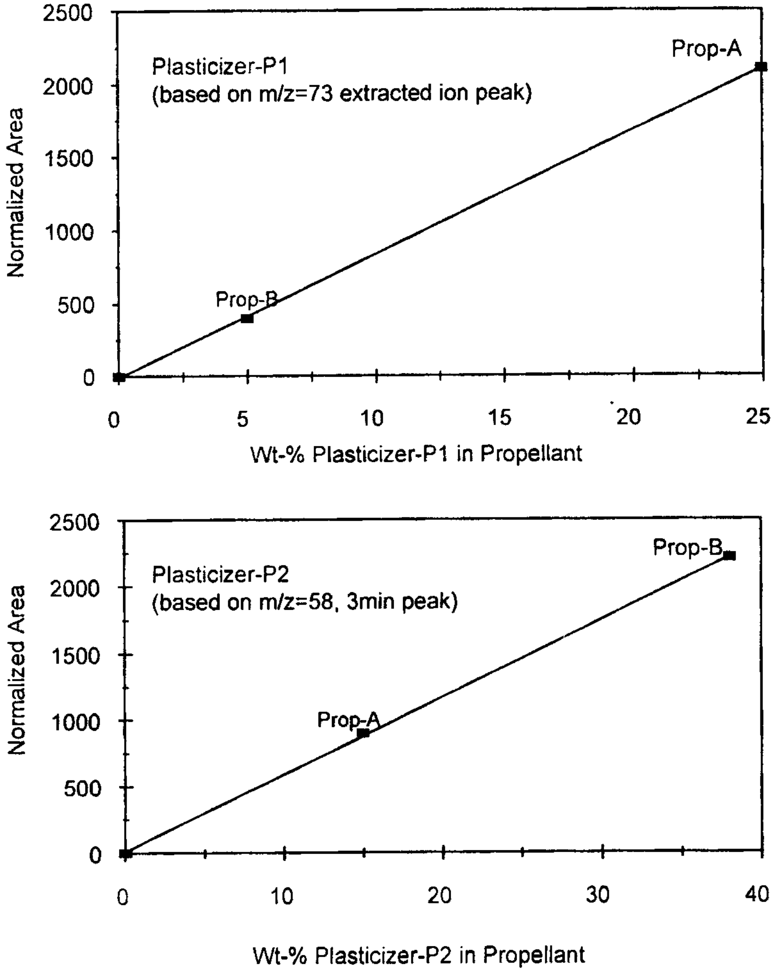


FIGURE 3

Calibration curves for determination of plasticizer profiles ("Prop-A" = Propellant-A; "Prop-B" = Propellant-B).

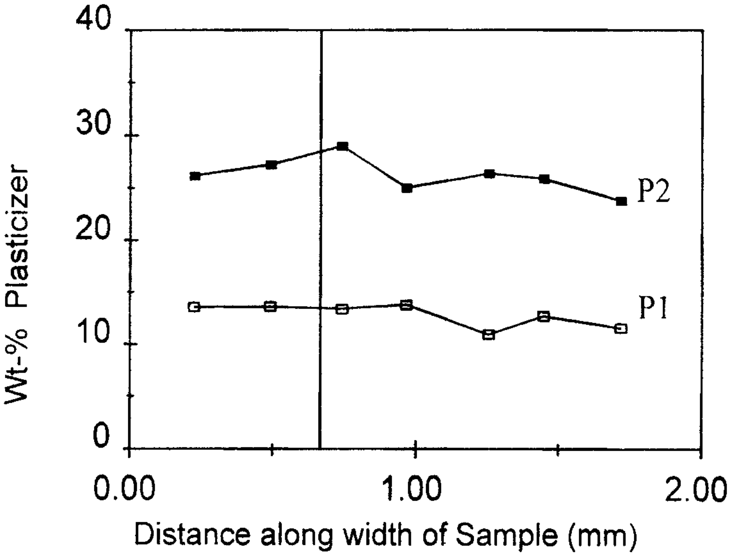


Figure 4

Experimentally determined concentration profiles for Plasticizer-P1 and Plasticizer-P2.

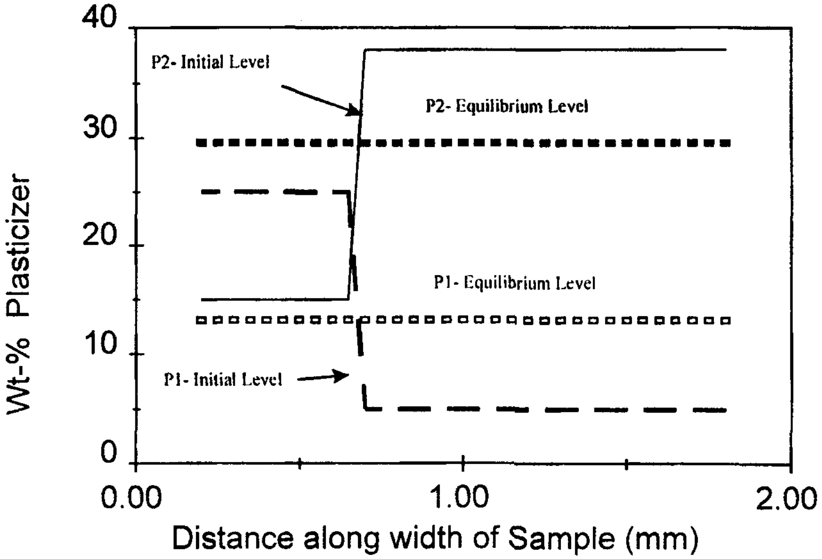
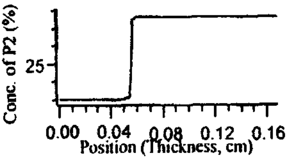
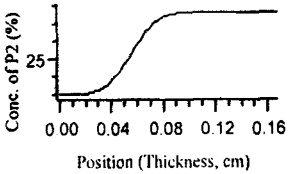
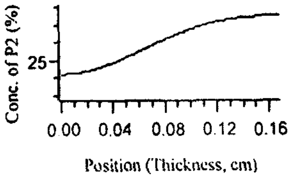
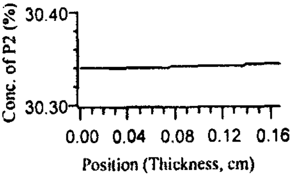


Figure 5

Theoretical concentration profiles for Plasticizer-P1 and Plasticizer-P2 under initial conditions and at equilibrium

Rate	Slow	Average	Fast	Concentration Profile
Diffusion Coefficient	10^{-12} cm^2/cm	10^{-11} cm^2/cm	10^{-10} cm^2/cm	Initial Profile 
Time to 10% Increase in Outer Layer Conc.	1.9 years	73 days	14.6 days	
Time to 50% Increase in Outer Layer Conc.	34.8 years	4.6 years	142.4 days	
Time to Equilibrium (see note)	792.7 years	79.27 years	7.927 years	

Note: Equilibrium is defined as the time when the difference between the maximum and minimum concentrations in the profile is less than or equal to 0.01%.

Figure 6

Calculated concentration profiles and times-to-equilibration.

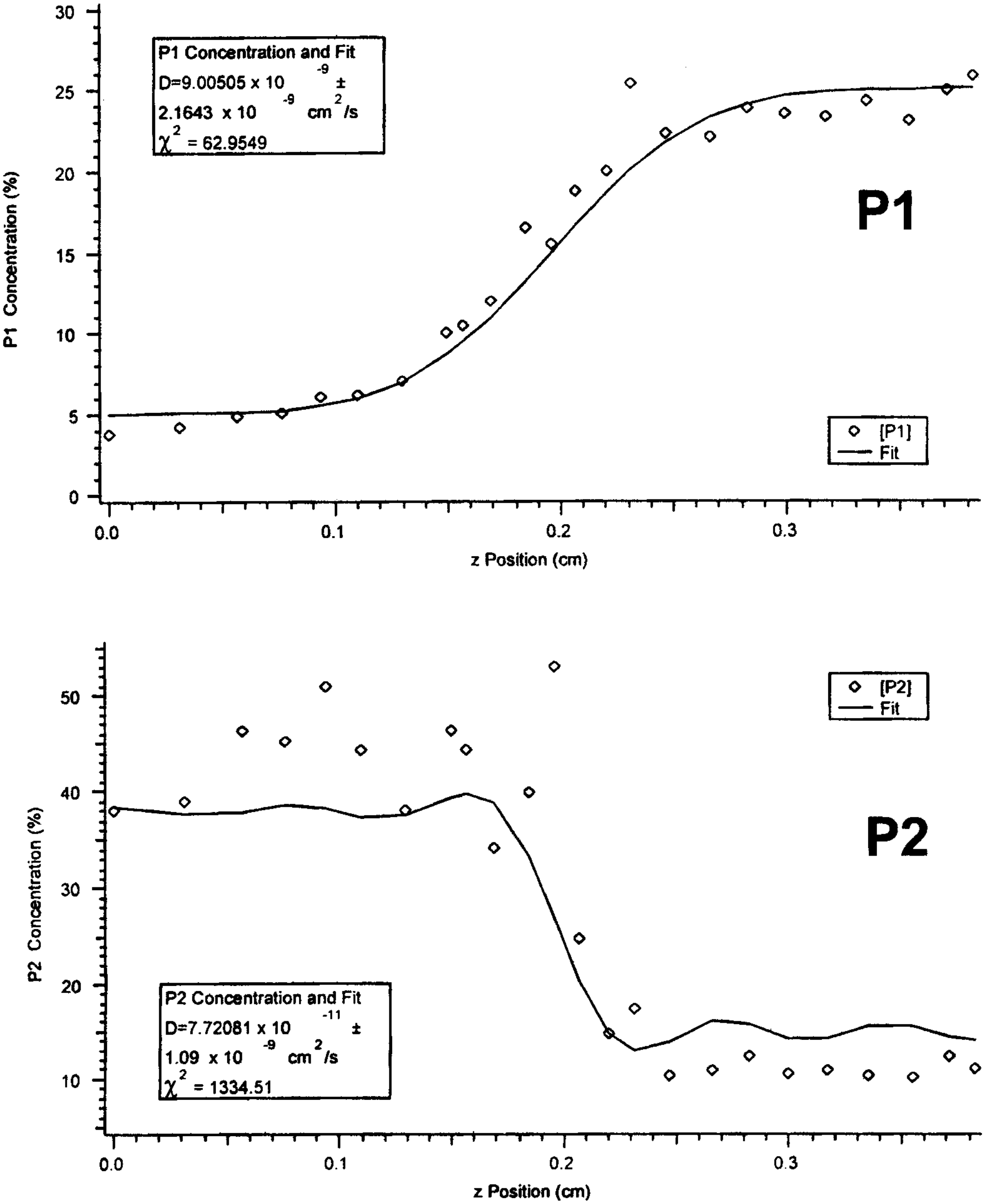


FIGURE 7

Experimental data and calculated fit for determination of diffusion coefficient.