THERMAL STABILITY OF FLUORESCENT DYES AS GEOTHERMAL TRACERS

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ABSTRACT

This work attempted to determine the effect of temperature on tbe fluorescence of rhodamine WT and fluorescein. 200 ppb solutions of rhodamine WT and 50 ppm solutions of fluorescein were subjected to 100, 150 and 200°C temperatures for a variable length of time. Reduction in relative fluorescence occurred in solutions of both rhodamine WT and fluorescein at all temperatures. The reduction in fluorescence is approximately a first-order reaction. It is most severe at 200°C. Rhodamine WT is more stable than fluorescein. Rhodamine WT solutions reached *50%* relative fluorescence at 200°C within 40 hours. After 150 hours, rhodamine WT becomes inactive at 200°C. However, at 150°C, the *50%* relative fluorescence is reached after 250 hours. Rhodamine WT solutions reached *50%* relative fluorescence after about 2000 hours at 100°C. Fluorescein solution lost its fluorescence after about three hours at 200°C. The relative fluorescence of fluorescein reached *50%* after about 20 and 150 hours at 150 and 100°C respectively. Hence, rhodamine WT can be used with confidence as a tracer in systems whose temperature is around 150°C. Rhodamine WT can also be used at 200°C in fractured geothermal reservoirs that admit short residence time. Fluorescein should be limited to low temperature systems, preferably around 100°C.

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1. INTRODUCTION

1.1 Introduction

Tracers are substances that can provide useful information about the media through which they flow. They must possess properties that can easily be detected and identified. A tracer that fluoresces can be identified by measuring its fluorescent activities. Color, mass and radioactivity are some of the properties that can be used to identify tracers. Tritium, a naturally occurring radioactive isotope of hydrogen, is often used as a tracer in the petroleum industry. Being radioactive, and hence a potential health hazard, tritium's utility is limited. Other tracers regularly used are the halides (Cl^-, Br^-, I^-), thiocynate, and methyl or ethyl acetate. Organic dyes, such as rhodamine, rhodamine WT and fluorescein are extensively used in tracing groundwater movement; of late they have also been used in both oil/gas and geothermal fields.

A basic and minimum information obtainable from a tracer test is the speed of first return between an injector and a producer, which gives an indication of connectivity between the two wells (Home, 1983). This information is useful in waterflood projects as well as in the reinjection of spent brines in geothermal fields. Reinjection of spent brines into a geothermal field is often the only environmentally acceptable means of disposing of this liquid which is produced in voluminous quantities. At the same time the reinjected fluid can maintain reservoir pressure. However, reinjection of relatively cold fluids can also have an adverse effect on the discharge enthalpy of the system. Because of the fractured nature of geothermal fields, the reinjected liquid has been observed to appear at the producing sites in a matter of hours after reinjection

(Horne,1982). Temperature equilibration in such a short residence rime is almost never achieved, resulting in the possible lowering of the system's enthalpy. A tracer test can establish the fluid pathways, within a reservoir, affording the operator a better understanding of the field.

Further information obtainable from a tracer study derives from a proposed model chosen to fit the observed concentration profiles between an injector and a producer. The convection–dispersion equation forms the basis for all the predictive models. This equation can be modified to account for changes in tracer as it flows through the medium, such as adsorption, ion exchange with the medium, or its chemical breakdown. The equation might also be based on some properties of the formation, such as fracture width. If the model can be made to fit the observed concentration profile, a quantitative estimate of these parameters can be made.

In quantitative work, the integrity of the tracer as it passes through the formation is important. Geothermal settings, with their characteristically high temperatures can alter the chemistry of tracers, thereby affecting the identifying property. Organic dyes are particularly susceptible to high temperatures, and their behavior with temperature is not well documented. In geothermal tracer tests, where a dye has been injected together with another tracer, the concentration profiles have sometimes indicated a low return of the dye. Tracer tests conducted in Svartsengi in 1984 used both rhodamine WT and potassium iodide (Gudmundsson and Hauksson, 1985). Figure 1 compares normalized relative recoveries of rhodamine WT and iodide during the Svartsengi test. Note that both curves reached peak concentration at the same time. The rhodamine WT curves drops sharply from the peak concentration to very low concentrations.

This sharp drop of concentration may indicate breakdown or adsorption of rhodamine WT (Gudmundson and Hauksson, 1985). Another tracer test that used rhodamine WT and potassium iodide was carried out in Klamath Falls in 1983 (Johnson, 1983). Figure 2 compares normalized relative recovery of rhodamine WT and iodide with time. The relative recovery of rhodamine WT compares favorably to the relative recovery of iodide in the Klamath Falls test. Again note the two curves attain *peak* concentration at the same time. Rhodamine WT relative concentration curve follows the same trend as the curve for iodide. Figures 1 and 2 illustrate an important point: rhodamine WT can produce a good match in one tracer test, and a poor one in another. The reason for this contradiction lies in the difference between the reservoirs' temperatures. The reservoir temperature in Svartsengi is in the region 235-240°C. Klamath Falls reservoirs have temperature of about 100°C. Clearly the higher temperature of Svartsengi field had affected rhodamine WT.

Despite the drawback of instability at higher temperature, organic dyes have some advantages over the more traditional tracers. Organic dyes, such as rhodamine WT, can be detected in small amounts. Rhodamine WT is detectable in concentrations of 13 ppb by using a filter fluorometer. Hence only small amounts of rhodamine WT are needed in a field test. Also rhodamine WT can be analyzed quickly and cheaply. A Turner filter fluorometer costs about $5000. The fluorometer is easy to use. It is small and sturdy and hence portable. We can use the fluorometer to measure the fluorescence of fluorescent dyes. We need a more elaborate counting instrument to analyze other tracers. For example, potassium iodide can be analyzed by ion chromatography technique. The ion chromatography equipment may cost upward of $25,000.

It takes about 20 minutes to get a single data point with this equipment (Gudmundson and Hauksson, 1985). It takes five minutes to get a similar data using a Turner filter fluorometer. Hence the overall cost associated with the use of rhodamine WT is small. Table 1 summarizes these cost benefits.

Another advantage of these dyes are their safety. Smart and Laidlaw (1971) discuss in length the toxicity of some of the dyes. They concluded that rhodamine WT and fluorescein are not toxic to life in the dosages employed in the field. Parker (1967) reported that rhodamine WT was not toxic to marine life. However, if these dyes are rendered unstable at high temperatures, their utility in geothermal setting is limited. This experimental work attempted to determine the effect of temperature on rhodamine WT and fluorescein.

1.2 The Scope and Objective of This Work

A host of factors affect the fluorescence of fluorescent dyes. These include temperature, solution pH, adsorption of dyes on the container walls, photochemical decay, etc. The presence of oxygen at higher temperatures may facilitate the oxidation of these dyes. This oxidation might alter their fluorescent activity. We limit our work to two dyes, rhodamine WT and fluorescein. This work attempts to determine the effect of temperature on the fluorescence of these dyes under the conditions where oxygen may be present. The solution pH is maintained between 5.0 and 5.5, the same as the pH of distilled water under atmospheric conditions. The effect of adsorption is neglected. Photochemical decay is briefly studied.

2. LITERATURE REVIEW

Fluorescent dyes have found extensive use as tracers in hydrology. Smart and Laidlaw (1977) mentioned several works in which these dyes have been used as tracers. The information derived from these tracer studies include such items as time of travel, quantitative estimate of longitudinal dispersion and transverse velocity in rivers, and establishing the flow paths in groundwater reservoirs. Rhodamine WT and fluorescein are the two tracers that were commonly used in these studies. Fluorescein and rhodamine have also been used in the oil industry. In a multiple tracer study to establish waterflood flow behavior, Burwell (1966) reported the use of fluorescein and rhodamine as two of the five tracers used. While tritium was assessed as probably the only practical tracer through a sand body over a long distance (300 to 1000 ft.), Burwell observed that since dyes are likely to adsorb onto a sand body, their appearance at the production end must indicate a highly permeable pathway. Ford (1966) lists two cases in which fluorescein was used as a tracer, and from which a directional fracture system was indicated. Sturm and Johnson (1950) reporting on a series of field experiments using chemical tracers in flood waters concluded that fluorescein possesses substantial advantages over the other two tracers (brine and surface active agents) because of its low cost, ease of injection and its detectability. Fluorescent dyes techniques have also been applied to geothermal fields. In 1979, fluorescein was used in Hatchobaru geothermal field in southern Kyushu, Japan. It was assessed that fluorescein could easily provide data on first arrival times (Horne,1982). In 1980, sodium fluorescein was used at a site near Valles Caldera in north central New Mexico, to esti-

mate, among other things, overall fracture volume (Tester et al., 1982). Fluorescein and rhodamine B have been employed as tracers in Raft River in south eastern Idaho and East Mesa in the Imperial Valley of Southern California (Capuano et al., 1983). Rhodamine WT, fluorescein and potassium iodide were used as tracers in the summer of 1983 in Klamath Falls, Oregon (Johnson, 1984). An injection-tracer test in Svartsengi field in Iceland (Gudmundsson and Hauksson, 1985) used rhodamine WT and potassium iodide. Results of the Klamath Falls test showed a low return for rhodamine WT compared to that of iodide; and results from Svartsengi field indicate the same discrepancy.

Fluorescent dyes are known to adsorb on sediments (Smart and Laidlaw, 1977). They also suffer certain changes in the presence of high temperatures. In porous media, adsorption is a major problem since a dye is exposed over a wide area; and the low temperature environment prevailing in groundwater systems renders temperature effects less of a problem. However, the same cannot be said of geothermal fields, or even of some hydrocarbon bearing systems. In fact, because of the fractured and high temperature nature of geothermal fields, the opposite is almost always true. Yet, of the works mentioned above in the use of fluorescent dyes as tracers in geothermal setting, only that at a site near Valles Caldera, actually tested the dye for its stability (Tester, 1982). Thermal degradation of a family of rhodamine dyes in their solid form (neither of which is rhodamine WT) is reported in two studies not related to tracer works. Rhodamine B chloride in solid form is reported to volatilize at temperature less than 200° C by dissociation into the neutral dye base and hydrogen chloride (Davie at al., 1974). A related solid compound, rhodamine 6G decomposes at 210° C (Taru and Takaoka, 1982). The lack of information on the thermal sta-

bility of these dyes demonstrates the need for basic research into this subject, especially since these dyes could be used in the place of more expensive chemicals in tracer studies.

3. PROPERTIES OF RHODAMINE WT AND FLUORESCEIN

Rhodamine WT and fluorescein are among the eight fluorescent dyes studied by Smart and Laidlaw (1977). The following is a summary of their findings.

As noted earlier, organic dyes have the advantage of being able to be detected in low concentrations. With the Turner 111 filter fluorometer, fluorescein can be detected in minimum concentration of 290 ppb and 13 ppb for rhodamine WT. One problem associated with the detection of these dyes is background fluorescence in natural waters. For dye solutions prepared in deionized distilled water, Smart and Laidlaw reported background readings (on a scale of 100 units) of 26.5 for fluorescein and 1.5 for rhodamine WT. We measured the background readings for every solution we tested. The background reading is subtracted from the fluorescence reading of the sample. This net fluorescence is the one that we are concerned with.

Fluorescence intensity varies inversely with the temperature of the dye solution at the time of its measurements. This variation is expressed in an exponential formula for a number of dyes. Therefore it is important to fix a base temperature to which all readings must be corrected. We chose 25°C as the base temperature in this work.

Smart and Laidlaw also investigated the effect of pH on the fluorescent activity of the dyes. They concluded that rhodamine WT is affected the most below pH 5.0, and suggested that some correction should be applied for dye solutions prepared in waters with a pH lower than 5.0. However, Stabro and Pyrch (1979) disagreed as they failed to observe the extensive decays for rho-

damine WT reported by Smart and Laidlaw.

During our work, we were careful not to expose the solutions to either artificial or sun light, in order to minimize photochemical decay. Smart and Laidlaw reported that decay rates are very high for fluorescein, less so for rhodamine WT. We were able to confirm this observation by exposing solutions of these dyes to both artificial and sun light for a number of days. There was little decay for rhodamine WT in artificial light, while fluorescein showed a noticeable decay. In sunlight, fluorescein showed a rapid decay within two days, while rhodamine WT had a half life of about 20 days.

In field application, fluorescence of a particular dye may be decreased as a result of a dye being adsorbed, or simply by the adsorption and scattering of light by the sediment particles. In the later case the dye is conserved but its fluorescent activity is masked; this is described as apparent background fluorescence by Smart and Laidlaw. One method of measuring the fluorescence of samples containing much sediments is simply to wait on them until they settled. However, Petri and Craven (1971) suggested that it might be helpful to dilute such sample before measuring their fluorescence. This eliminates the time spent to wait on dye sample containing much sediments. This method is useful when the effluent concentration is needed to adjust the injection volume.

In the case of actual dye loss as a result of adsorption, quantification is difficult and Smart and Laidlaw (1977) suggested that it was better to choose a dye most resistant to adsorption. Both rhodamine WT and fluoresceine have moderately high resistance to adsorption.

4. EXPERIMENTAL PROCEDURE

4.1 Preparation of Solutions

Following the suggestion by Wilson (1968) that at least 10 gm of a dye should be used to make a stock solution, we measured 10.00 gm of a dye in a chemical balance and introduced it in a 1000 ml flask. We added to it deionized triply distilled water to the 1000 ml mark. The flask was then stoppered and gently inverted several times to completely dissolve the dye. We transferred the solutions to a dark brown 1000 ml bottle and capped the bottle. The bottle was then stored in a dark cabinet. The concentration of the stock solution is 10,000 ppm if the dye is fluorescein; the concentration of rhodamine WT stock solution is 2,000 ppm (rhodamine WT original solution was 20% strenght). Solutions of lower strengths were prepared fkom successive dilution of the stock. For example, to prepare 200 ppb solution of rhodamine WT, we pipetted out 10 ml of stock into a 1000 ml flask, topped the flask to the 1000 ml mark with deionized distilled water to produce a solution of 200 ppm strength. 10 ml of 20 ppm solution were then pipetted into another 1000 ml flask and topped with distilled water to make a solution of 200 ppb . The find solution was prepared in duplicate and transferred into labeled dark brown bottles. We immediately measured their fluorescence. One of these solutions was used as a control. Both solutions were stored in a dark cabinet. In the case that more than 1000 mL of a solution was needed, a new pair of solutions would be prepared from the original stock, having discarded the intermediate dilutions. Because light affects the fluorescent activity of these dyes, we took care to work in semidarkness when solutions were being prepared or when they

were on the bench.

4.2 Heating up the Solutions

With the room in semidarkness, we removed the solutions from the cabinet. 5 ml or so were transferred into a standard cuvette and its fluorescence measured at a fluorometer aperture setting that gave maximum reading on fluorometer dial. This setting was achieved by adjusting the amount of the light passing through the primary filter, and/or using neutral density filters. After the reading had stabilized it was noted down; the cuvette was removed from the fluorometer and the temperature of the sample was taken by a mercury in glass thermometer. We noted that opening the door of the chamber of the fluorometer momentarily caused the fluorometer to indicate a higher reading. Thus we repeatedly opened and shut the door until the reading stabilized, say after three openings. This reading together with the temperature of the sample were recorded in a special form made up to record trial number, solution strength, fluorometer readings, sample temperature, etc. The sample was discarded and a new one was measured the same way. This procedure was carried out for both working and control solutions (of a particular strength). These readings form the calibration for that solution. Next the background fluorescence of the distilled water used in solution preparation was measured at the same fluorometer setting. This was recorded together with its temperature. Next the teflon cups previously washed with detergent and rinsed several times with deionized water were rinsed with small volumes of the solution. The teflon cups are then filled with approximately 20 ml of the solution. The experiment at a temperature would begin with 10 or 12 of these cups. The cups

were capped with teflon discs and inserted in aluminum jackets. The tops of the jackets were screwed on by hand and tightened gently in a vice with a wrench. We transferred the jackets into a preheated oven at the temperature of interest. We noted down the time. A pair of the containers was removed from the oven at predetermined intervals as fast as possible to minimize a fall in temperature of the oven. We immediately quenched the containers under tap water. When cold they were unscrewed and the teflon disc examined for possible leaks. If a leak was indicated the contents of the container was discarded. The fluorescence of the content of each container was measured at least twice, their temperature taken, and these readings together with the time at which the containers were removed from the oven were recorded.

4.3 Sample Containers

Two types of containers were used. The first type consists of teflon cups. These are about four inches long, half an inch across, and one quarter of an inch in thickness. They are shaped like cylinders, having a rim one quarter of an inch thick. The cups were drilled out of pieces of solid teflon. To use them, they are inserted into aluminum jackets of approximate inside dimensions, The jackets are fashioned with about eight treads in which a top piece is screwed. The rim of the cup hold the cup at the mouth of the jacket. A teflon disc about an eighth of an inch thick and a little over half of an inch across, cut from a teflon sheet, seals the mouth of the cup.

The second type of the containers are made up of stainless steel. Their insides were specially coated with teflon by Con-Val of Oakland, Ca. They are shaped like miniature flasks with both ends open. The ends have about six in-

side treads which accepts stainless steel plugs. The plugs are wrapped with teflon ribbon. They are screwed to both ends of flasks. The volume of these flasks is about 75 ml.

Another type of containers used initially were the aluminum jackets lined with gold. These were discarded *after* we found out that the gold acted as a catalyst in the bleaching of rhodamine WT.

4.4 The Air Baths

Two air baths were used at USGS facilities at Menlo Park. These are of "Blue M" type that can heat up to about 600° C. Although they have temperature gauges, we hung mercury thermometers inside the ovens. There was some discrepancy between the temperatures indicated by the two instruments. For recording purposes we used the thermometer readings. The temperature reading from the gauge was monitored by a clock driven paper chart temperature recorder. In this way we made sure that any temperature fluctuations and current interruptions were recorded.

4.5 Measuring Instrument

SEQUOIA-TURNER MODEL 112 DIGITAL FILTER FLUOROMETER with standard Sample Door was used to measure fluorescence of both rhodamine WT and fluorescein. Excitation energy was provided by a Far Ultra Violet U tube mercury lamp #110-851. This mercury lamp has major emission at 254nm, with useful output at the 297, 313, 405, 436 and 546nm wavelengths (see Installation and Operating Manual for Turner Filter Fluorometer, Model 112). The following combinations of Primary and Secondary filters were

chosen.

Rhodamine WT: *Primary* Filter **#110-822(58);** Secondary Filter **#110-824(23A).**
Fluorescein : *Primary* Filter **2A + #110-813;** Secondary Filter **#110-818(2A-12).**

Rhodamine WT has excitation and emission maxima at ***555*** nm and **580** nm. The values for fluorescein are **490** nm and **520** nm (Smart and Laidlaw, **1977).** We used rounded cuvettes, **12 x 75 mm,** to hold the solutions when measuring the fluorescence. We thoroughly cleaned the cuvettes with detergent every time we **used** them. We rinsed the cuvettes with the solution whose fluorescence was to be measured.

4.6 Rhodamine WT and Fluorescein

Rhodamine WT and fluoresecein dyes were bought from Keystone-Ingham Corp. of Santa Fe Springs, California. Rhodamine WT came in a plastic bottle in a liquid form of **20%** strength. Rhodamine **WT** Product Number was **703-010-277.** Fluorescein came in a tin in the form of **dark brown** crystals. Fluorescein Product Number was **801-073-559** and Lot Number **L3041.**

5. RESULTS

Two tracer tests were conducted in Klamath Falls in the summer of 1983. Rhodamine WT was used as one of the tracers. Rhodamine WT return concentration in the test was in the region of a few parts per billion. Therefore we decided to test the stability of Rhodamine WT solution at 200 ppb. Fluorescein was tested at 50 ppm. Section 4.2 outlines the data collection procedure. The base temperature of 25°C was chosen for fluorescence measurements. Smart and Laidlaw (1977) give an empirical formula to correct data to base temperature:

$$F_s = F_0 e^{n(T_s - T)} \tag{5.1}$$

where F_s is the fluorescence reading at base temperature T_s, F_0 is the fluorescence reading at sample temperature T, and n is a constant for a given dye: n is $-0.027°C^{-1}$ for rhodamine WT and $-0.0036°C^{-1}$ for fluorescein. The above formula was applied to all fluorescence readings. The fluorescence reading before the solution was heated up is taken as the basis for calculating the relative concentration in that run.

Tables 2, 3 and 4 show the relative fluorescence readings for rhodamine WT. Relative fluorescence readings for fluorescein are shown in Tables 5, 6 and 7. Rhodamine WT data are graphed in Figures 3 through 8, and those for fluorescein in Figures 9 through 12. The data for both dyes show some scattering resulting from the lack of experimental control and occasional erratic behavior of the fluorometer. The fluorometer was left on all the time to stabilize it. Nevertheless, even this precaution was not enough to guarantee consistent readings all the time. Initially, we used aluminum containers to hold the

solutions. The containers had a gold coat applied inside them. However, we stopped using these containers after realizing that gold was acting as a catalyst in the bleaching of rhodamine WT. We used teflon cups and teflon coated stainless steel containers described in section 4.3. We lost experimental control as a result of using teflon pressure containers. We would ideally like to keep the same experimental conditions, such as container and sample volumes, etc. in all runs. However, this was impossible since the teflon cups deformed with temperature and pressure. As a result, no one run had the same conditions as the other. The curves for the relative fluorescence reflect this lack of experimental control. Higher fluorescence readings occurred at later times, resulting in a zig zag profile. We graphed the time axis on a logarithmic scale to properly show all the data, keeping the vertical axis for relative fluorescence cartesian. The absolute fluorescence readings for rhodamine WT and fluorescein can be estimated from their calibration curves prepared for concentrations from 1 to 200 ppb for rhodamine WT and 10 to 50 ppm for fluorescein. These are shown in Tables 8a and 8b for rhodamine WT. Table 9 shows calibration data for fluorescein. The calibration data are graphed in Figures 13 and 14 for rhodamine WT, and Figure 15 for fluorescein. The same filter combinations described in section 4.5 were used. The lower concentration curve (Figure 13) was determined at 10X aperture setting of the fluorometer, and that for higher concentrations (Figure 14) at 1X aperture setting. The calibration data for fluorescein was measured at 3X aperture setting. The aperture settings come in four selections in the Turner Flourometer 112: 1X, 3X, 10X or 30X. Larger aperture setting gives more sensitivity. The desired sensitivity to the emitted light can be controlled by using neutral density filters. These are rated by the

mount of emission they transmit: a 10% neutral density filter allows only 10% of emitted light through, etc. We used a 10% neutral density filter for all our measurements for rhodamine WT and a 1%neutral density filter for fluorescein. The calibration curves for both rhodamine WT and fluorescein are linear in all concentrations tested. Care was taken not to expose the solutions to light throughout our work. Tables 10a and 10b, and Figures 16a and 16b show the photochemical decay data for rhodamine WT at *200* ppb and fluorescein under indoor and outdoor conditions. All solutions were kept in transparent bottles. The indoor solutions were exposed to direct fluorescent light for the time of the experiment. Rhodamine WT solution kept indoors showed little decay. Rhodamine WT solution kept outdoors was exposed to direct sunlight during the length of the experiment. Rhodamine WT solution kept outdoors showed a half life of 360 days. We can use properly kept rhodamine WT solution for a long time as decay under fluorescent light is slow (see Figure 16a). We kept our solutions in brown bottles stored in a dark cabinet. However, fluorescein solutions need more care. Fluorescein solution kept indoors has a half life of 225 hours. Fluorescein solution kept outdoors was initially exposed to direct sunlight for six hours. During this time, fluorescein suffered about 50% reduction in relative fluorescence. After six hours under direct sunlight, fluorescein solution was transferred to a shaded place. It was kept there for the duration of the experiment. See figure 16b.

The relative fluorescence data for rhodamine WT shown in Tables 2, 3 and 4, and Figures 3 through 5 were averaged out to give a single relative fluorescence curve at each temperature. These average values are graphed in Figures *6*, 7 and 8 at temperatures 100, 150 and 200°C respectively. The data

points are connected to emphasize the difficulty of obtaining consistent results. We removed the erratic data, and analyzed the more consistent data using first-order reaction kinetics (see Appendix A). Figures 13 through 15 show the natural logarithm of relative fluorescence of rhodamine WT against time in hours. Figures 16 through 18 show the natural logarithm of relative fluorescence of fluorescein against time in hours. We were able to fit a straight line through the data for Figures 13 through 18 by the method of least squares. The statistical data relating to the goodness of the fit for the six cases are shown in Table 16. As can be seen from Table 16 the correlation coefficient, which is a measure of how good the fit is, ranges from 0.95 to 0.93 for rhodamine WT. The correlation coefficient for fluorescein is in the range 0.95 - 0.51. Fluorescein data did not correlate well. We can get first-order rate constants for rhodamine WT from Figures 13, 14 and 15 at 100, 150 and 200°C respectively by determining the slope of the curves. The first-order rate constants relate reduction of relative fluorescence of the dye with time. The first-order rate constants for fluorescein can be similarly determined from Figures 16, 17 and 18 at 100, 150, and 200°C respectively. Table 17 summarizes the first-order rate constants for rhodamine WT and fluorescein. Note in Table 17 that the first-order rate constants for fluorescein are one order of magnitude greater than those for rhodamine WT at the three temperatures. The larger reaction constants indicate that fluorescein is more active, and hence less stable than rhodamine WT. We graphed the natural logarithm of first-order rate constants for rhodamine WT and fluorescein against temperature in Figure 19 and obtained a linear relationship. Figure 19 enables us to read off first-order rate constants for rhodamine WT and fluorescein at any temperature between 100 and 200°C.

The first-order rate constants for rhodamine WT (Figures 13-15) indicate that rhodamine WT suffers 50% reduction in relative fluorescence during the first 40 hours at 200°C. At 150°C, the relative fluorescence of rhodamine WT is reduced to 50% after 150 hours. Rhodamine WT reaches 50% relative fluorescence at 100°C after about 2000 hours.

The first-order rate constants for fluorescein (Figures 16-18) indicate that fluorescein becomes inactive after only three hours at 200°C. At 150°C, fluorescein reaches 50% relative fluorescein after 20 hours. And at 100°C, fluorescein attains 50% relative fluorescein after 150 hours.

6. DISCUSSION AND CONCLUSION

As mentioned in the introduction, very little is known about the stability of fluorescent dyes. Thus, this research was undertaken to fill some of that gap. In particular, we wanted to study the thermal stability of rhodamine WT and fluorescein. But a host of other factors affect the fluorescent behavior of these dyes. Smart and Laidlaw (1977) list the solution pH, adsorption on the substrate, photochemical decay as some of the factors to be accounted for in the study of these dyes. These factors may have a more adverse effect on the fluorescence of the dyes at higher temperatures. We took the precaution against photochemical decay and kept the solution pH at the pH of deionized distilled water. We made no attempt to control our experiment with respect to adsorption or ensuring inert atmosphere for the tests. We used teflon cups or teflon coated stainless steel cylinders throughout our work. These containers deteriorated with reuse. Thus quantifying adsorption was difficult. The combination of pH and oxygen at elevated temperature may have some impact on the fluorescence results (Counsil, 1986). A better controlled experiment is needed to establish the fluorescence data of rhodamine WT and fluorescein at the temperatures considered in this work.

Though limited, our work shows that rhodamine WT is more stable than fluorescein. Rhodamine WT can be used for test periods as long as a month provided the temperature of the system is no more than 150°C. Rhodamine WT can be used in fractured systems even at 200°C. The rate of return of tracers in fractured reservoirs is high. The resident time of tracers can be very short (Home, 1982). Under these conditions, rhodamine WT can be used with some confidence at 200°C. Fluorescein, on the other hand, should be limited to

low temperature systems, preferably around 100°C.

The results obtained in this work indicate that fluorescein is less stable than rhodamine WT. This conclusion was reached by considering first-order reaction rates of rhodamine WT and fluorescein (see Table **17).** Our experimental data shows that the reduction of relative fluorescence of rhodamine WT and fluorescein in the concentrations tested (200 ppb and 50 ppm for rhodamine WT and fluorescein respectively) **is** first-order reaction. For each dye and at each temperature, we calculated its first-order reaction constants. First-order reaction constants have some application in analyzing geothermal tracer tests. Various models have been proposed to analyze tracer returns from geothermal reservoirs (Fossum and Horne, **1982;** Jensen and Home, **1983;** Home and Rodriguez, **1983** and Walkup, **1984).** Retention of tracer in reservoir **rocks** makes successful application of these models difficult. The process producing tracer retention may include adsorption, diffusion, dissolution and ion exchange (Jensen and Home, **1983).** Adsorption as well as diffusion are accounted for in some models (Jensen and Home, **1983** and Walkup, **1984).** Accounting for tracer dissolution can improve the performance of the model considerably. Dissolution of a tracer is characterized by its reaction constant. First-order reaction constants such as found in this work for rhodamine WT and fluorescein can be used in the formulation of the model. If the model is linear, the first-order reaction constants need not be incorporated in the model itself. The return concentration profile can be corrected by shifting it upward along the concentration axis by an amount determined by the first-order reaction constant of the dye tracer. The model can then be applied to the corrected concentration profile. However, if the model is non-linear, a product of relative concentration

(fluorescence) and the first-order reaction constant of the dye must be introduced into the model as a sink term (*Grisak* and Pickens, 1980). Since the reaction constants are determined for some discreet temperature, we must exercise care to use the correct constant. We obtained approximations of first-order reaction constants for rhodamine WT and fluorescein for temperatures between 100 and 200°C. Figure 19 can be read to give first-order reaction constants for rhodamine WT and fluorescein at temperatures between 100 and 200°C.

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TABLES

Table 1. Comparison Between Rhodamine WT and Potassium Iodide Svartsengi Tracer Test*

Tracer	Rhodamine WT	Potassium Iodide
Amount Injected, Kg	40	350
Analysis Technique	Fluorometry	Ion Chromatography
cost of Equipment, $	5000	25000
Analysis Time Per Sample, min.	2	20

* Gudmundsson and Hauksson, 1985.

Table 2. Relative Fluorescence of Rhodamine WT (200 ppb) at 100°C.
(10% Neutral Density Filter, 1X Aperture)

	Relative Fluorescence, %*			
Time, hr.	Run 1	Run 2	Run 3	Run 4
24	85.0	86.0	85.0	
48	90.5	89.0	76.0	76.0
72	89.0	92.5	92.5	91.0
168	86.0	87.5		
672	79.0	79.0	78.0	78.0

* Initial Readings in Fluorescence Units :
Run 1 : 81.0
Run 2 : 81.0
Run 3 : 78.0
Run 4 : 79.0

Table 3. Relative Fluorescence of Rhodamine WT (200 ppb) at 150°C.
(10% Neutral Density Filter, 1X Aperture)

	Relative Fluorescence, %*			
Time, hr.	Run 1	Run 2	Run 3	Run 4
1	97.0	98.0	100.0	98.0
2	89.0	74.5	94.0	87.0
12	95.0	84.5	97.0	80.5
18	77.5	94.5	74.0	89.0
24	72.5	90.0	75.5	81.5
36	56.5	47.0	74.0	72.5
46	80.0	81.0	72.5	75.0
72	64.0	65.0	66.0	65.0
172	66.0	64.5	64.5	

* Initial Readings in Fluorescence **Units:**
Run 1 : 79.5
Run 2 : 76.5
Run 3 : 78.5
Run 4 : 80.5

Table 4. Relative Fluorescence of Rhodamine WT (200 ppb) at 200°C.
(10% Neutral Density Filter, 1X Aperture)

	Relative Fluorescence, %*			
Time, hr.	Run 1	Run 2	Run 3	Run 4
1	85.5	95.5	88.0	98.0
2	72.0	68.0	72.5	68.5
6	66.0	65.0	70.0	66.0
18	37.0	20.5	42.0	21.5
24	22.5	22.5	35.0	31.5
36	59.0	44.5	60.0	45.0
48	45.0	52.5	46.5	54.5
50	24.0	33.5	21.0	29.0
52	12.5	27.0	11.5	25.0
76	7.0	5.5		
144	9.0	9.0	4.5	

* Initial Readings in Fluorescence Units:
Run 1 : 80.0
Run 2 : 76.5
Run 3 : 80.0
Run 4 : 81.0

Table 5. Relative Fluorescence of Fluorescein (50 ppm) at 100°C.
(1% Neutral Density Filter, 3X Aperture)

Time, hr.	Relative Fluorescence, %*
1	73.0
7	56.0
15	57.5
116	45.5
146	46.0
163	42.5
192	46.5
287	45.5
358	46.0
361	51.5
456	51.5
478	50.0
501	49.5

* Initial Reading: 81.0 Fluorescence Units

Table 6. Relative Fluorescence of Fluorescein (50 ppm) at 150°C.
(1% Neutral Density Filter, 3X Aperture)

	Relative Fluorescence, %*	
Time, hr.	Run 1	Run 2
1	73.5	78.0
2	48.0	79.0
3	46.0	59.5
4	45.0	64.5
5	45.5	60.5
6	41.5	39.5
10	40.0	
14		56.5
15	40.5	
16		50.5
18	50.0	50.0
21		40.0
24	39.0	30.5
28		31.0
48	27.0	
72	18.5	
144	19.5	31.5
192		27.5
288		30.0
312		31.0

* Initial Readings in Fluorescence Units:
Run 1 : 79.5
Run 2 : 81.0

Table 7. Relative Fluorescence of Fluorescein (50 ppm) at 200°C.
(1% Neutral Density Filter, 3X Aperture)

Time, hr.	Relative Fluorescence, %*	ln(Rel. fl.)
1	53.5	3.9797
2 .	29.5	3.3844
3	5.0	1.6094

Initial Reading: 77.0 Fluorescence **Units**

Table 8a. Calibration Data for Rhodamine WT at 25°C
(10% Neutral Density Filter, 10X Aperture)

Concentration, ppb	Fluorescence, Fluorescence units
1	5.5
2	12.5
4	20.5
6	30.0
10	44.0

Table 8b. Calibration Data for Rhodamine WT at 25°C
(10% Neutral Density Filter, 1X Aperture)

Concentration, ppb	Fluorescence, Fluorescence units
10	4.0
20	9.5
40	19.5
60	27.0
80	35.5
100	42.0
200	81.0

Table 9. Calibration Data for Fluorescein at 25°C
(1% Neutral Density Filter,3X Aperture)

Concentration, ppm	Fluorescence, Fluorescence units
10	16.0
20	30.0
30	49.0
40	63.0
50	81.0

Table 10a. Photochemical Decay of Rhodamine WT (200 ppb)
(10% Neutral Density Filter, 1X Aperture)

Rhodamine WT				
	Outdoors'		Indoors[2]	
rime, hr.	Rel. fl.[3], %*	ln(Rel. fl.)	Rel. fl.,%*	ln(Rel.fl.)
0	100.0	4.6052	100	4.6052
24			98.0	4.5850
43	93.0	4.5326	96.0	4.5643
138	74.0	4.3041	94.0	4.5433
161	70.0	4.2485	94.0	4.5433
212	67.0	4.2047	91.0	4.5109
310	66.0	4.1897	94.0	4.5433
335	54.0	3.989	91.0	4.5109
359	49.0	3.8918	90.0	4.4998
409	47.0	3.8501	88.0	4.4773
433	41.0	3.7136	88.0	4.4773
457	39.0	3.6636	88.0	4.4773
530	38.0	3.6376	86.0	4.4543
554	32.0	3.4657		
,672	26.0	3.2581		

1. **Exposed** to direct sunlight .
2. **Exposed** to a fluorescent light .
3. Rel. fl.: Relative Fluorescence.

* Initial Reading: 79.5 Fluorescence Units

Table 10b. Photochemical Decay of Fluorescein (50 ppm)
(1% Neutral Density Filter, **3X Aperture**)

Fluorescein				
	Outdoors[1]		**Indoors**[2]	
rime, hr.	Rel. **fl.**[3], %*	ln(Rel. fl.)	Rel. fl.,%*	ln(Rel.fl.)
0	100.0	4.6052	100	4.6052
6	92.4	4.5261	49.6	3.9040
20	88.5	4.4830	47.3	3.8565
25	87.2	4.4682	40.9	3.7111
31	84.3	4.4344	30.5	3.4177
43	85.8	4.4520	30.5	3.4177
56	82.7	4.4152	30.5	3.4177
69	78.2	4.3593	22.9	3.1311
94	74.7	4.3135		
107	69.2	4.2370	20.5	3.0204
130	65.3	4.1790	18.6	2.9232
154	62.7	4.1384	17.3	2.8507
180	57.6	4.0535	16.1	2.7788
161	51.5	3.9416	12.6	2.5337

1. Kept outside under a shade .
2. Exposed *to* a fluorescent light .
3. Rel. fl.: Relative Fluorescence.

* Initial Reading: **78.5** Fluorescence Units

Table 11. Relative Fluorescence of Rhodamine WT (200 ppb) at 100°C.
(10% Neutral Density Filter, 1X Aperture)
(Selected Data)

Time, hr.	Relative Fluorescence, %*	ln(Rel. fl.)
1	100.0	4.6052
72	97.5	4.5747
168	94.5	4.5486
672	79.0	4.3694

* Average Initial Reading: 80.0 Fluorescence Units

Table 12. Relative Fluorescence of Rhodamine WT (200 ppb) at 150°C.
(10% Neutral Density Filter, 1X Aperture)
(Selected Data)

Time, hr.	Relative Fluorescence, %*	ln(Rel. fl.)
1	100.0	4.6052
12	97.0	4.5742
18	94.5	4.5486
24	90.0	4.4998
46	81.0	4.3944
172	66.0	4.1897

* Average Initial Reading: 79.0 Fluorescence Units

Table 13. Relative Fluorescence of Rhodamine WT (200 ppb) at 200°C.
(10% Neutral Density Filter, 1X Aperture)
(Selected Data)

Time, hr.	Relative Fluorescence, %*	ln(Fl. rel.)
1	98.0	4.5850
2	72.5	4.2836
6	70.0	4.2485
36	60.0	4.0943
48	54.5	3.9982
50	33.5	3.5115
144	9.0	2.1972

* Average Initial Reading: 79.5 Fluorescence Units

Table 14. Relative Fluorescence of Fluorescein (50 ppm) at 100°C.
(1% Neutral Density Filter, 3X Aperture)
(Selected Data)

rime, hr.	Relative Fluorescence, %*	ln(Rel. fl.)
1	73.0	4.2905
7	56.0	4.0254
15	57.5	4.0518
116	45.5	3.8177
146	46.0	3.8286
163	42.5	3.7495
192	46.5	3.8395
287	45.5	3.8177
358	46.0	3.8286

* Initial Reading: 80.0 Fluorescence Units

Table 15. Relative Fluorescence of Fluorescein (50 ppm) at 150°C.
(1% Neutral Density Filter, 3X Aperture)
(Selected Data)

Time, hr.	Relative Fluorescence, %*	ln(Rel. fl.)
2	79.0	4.3694
4	64.5	4.1667
14	56.5	4.0342
18	50.0	3.912
21	40.0	3.6884
24	39.0	3.6636
48	27.0	3.2958
72	18.5	2.9178

* Average Initial Reading: 80.0 Fluorescence Units

Table 16. Correlation Coefficients for Rhodamine WT and Fluorescein

	Correlation Coefficients	
Temperature, °C	Rhodamine WT	Fluorescein
100	*0.99*	0.51
150	0.93	0.95
200	*0.95*	0.74

Table 17. Reaction Constants, k , for Rhodamine WT and Fluorescein

Temperature °C	Rhodamine WT		Fluorescein	
	k, per hr.	ln(k)	k, per hr.	ln(k)
100	0.0003476	-8.0948	0.0009803	-6.9276
150	0.002353	-6.0521	0.01965	-3.9298
200	0.01547	-4.1690	1.1852	0.1699

Table 1A. First-order Reaction Rate Data for Rhodamine WT

Temperature, °C	A	k	R
100	99.7	0.0003476	0.99
150	96.5	0.002353	0.93
200	88.2	0.01547	0.95

Table 1B. Correlation Constants for Rhodamine WT

a_1	a_2	b_1	b_2
113.8145	0.000007849	0.001225	0.03756

FIGURES

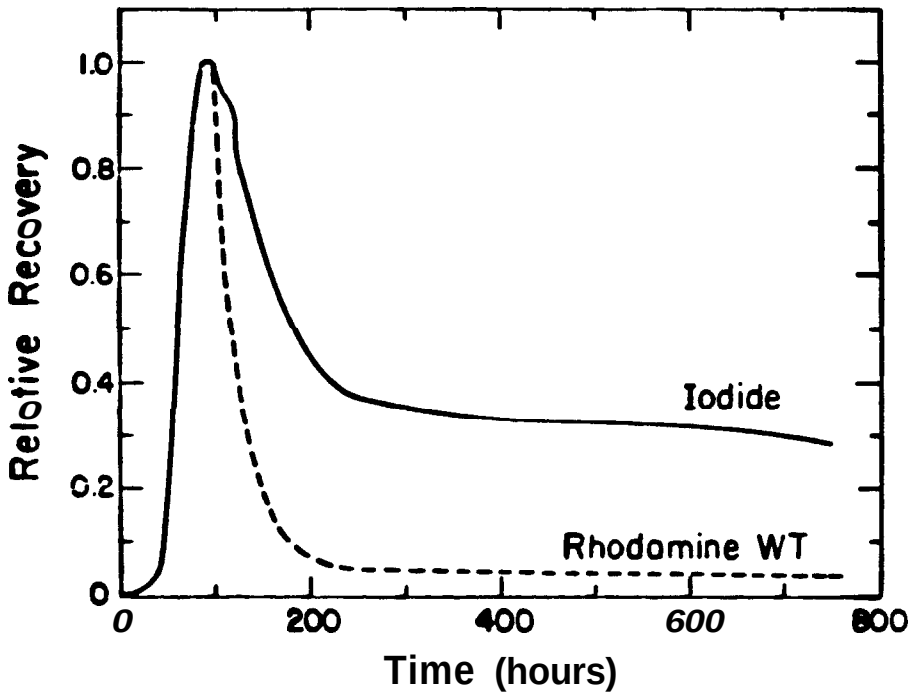

FIGURE 1. Relative Recovery of Rhodamine WT and Iodide during Svartsengi Tracer Test (Gudmundsson and Hauksson, 1985)

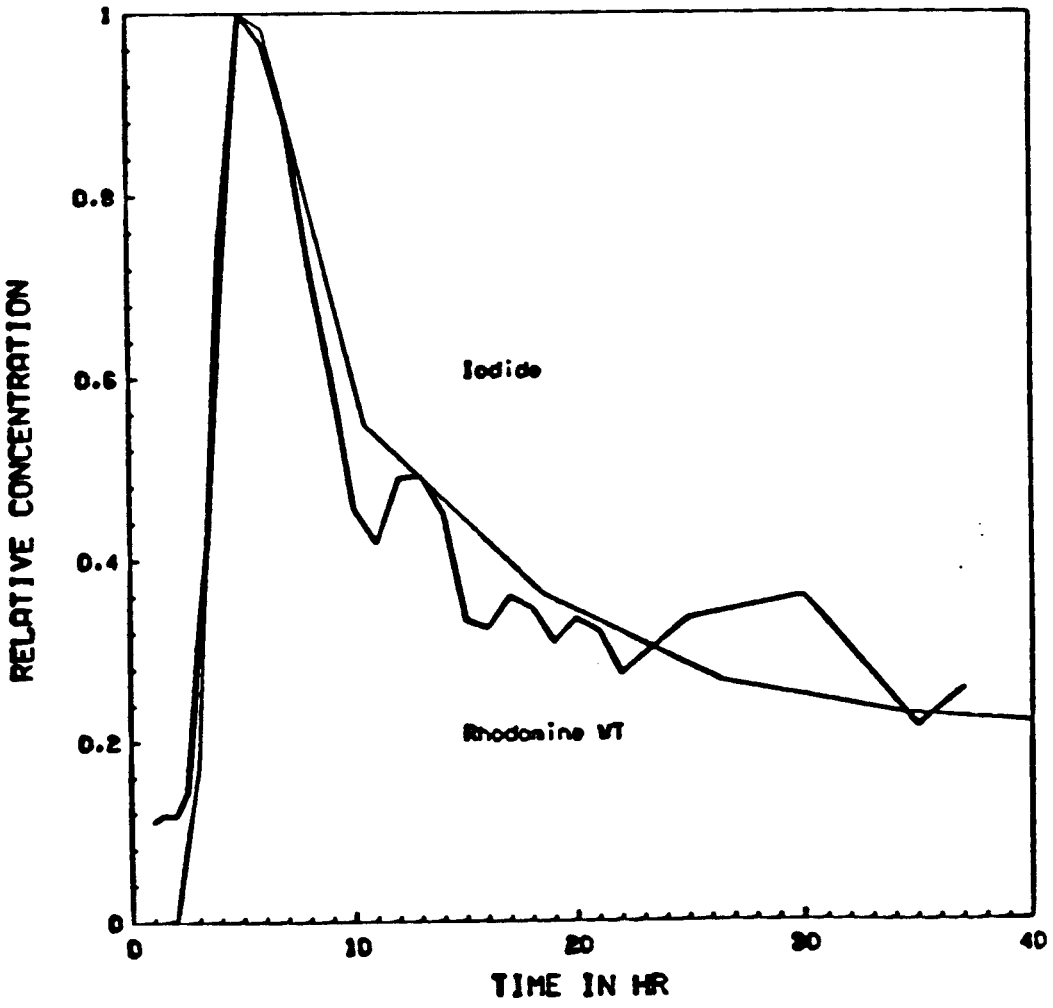

FIGURE 2 Relative Recovery of Rhodamine WT rod Iodide During Klamath Falls Tracer Test (Johnson, 1984)

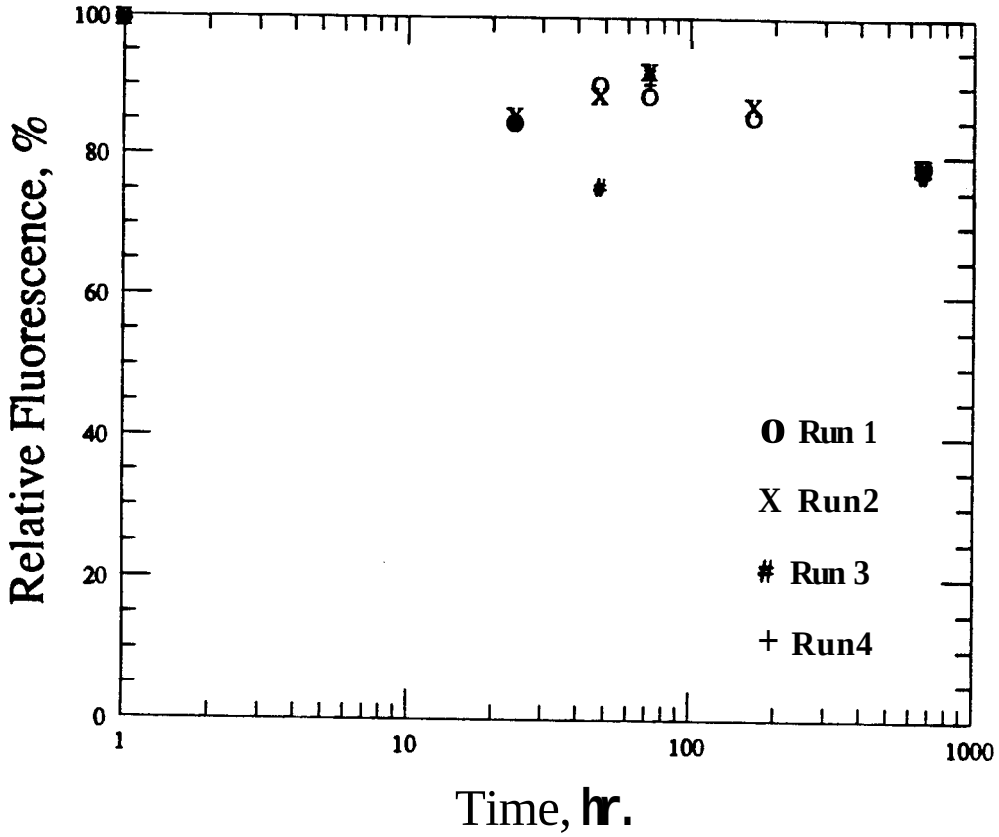

Figure 3: Relative Fluorescence vs. Time for Rhodamine WT (200 ppb) at 100°C.

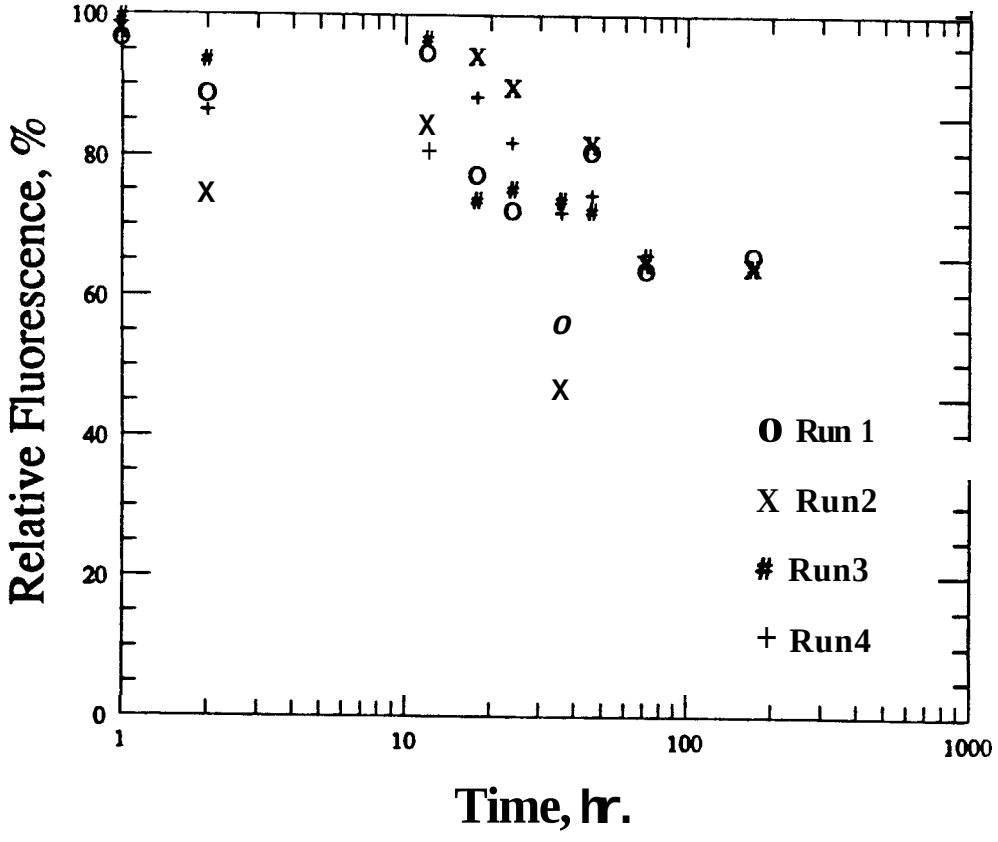

Figure 4: Relative Fluorescence vs. Time for Rhodamine WT (200 ppb) at 150°C.

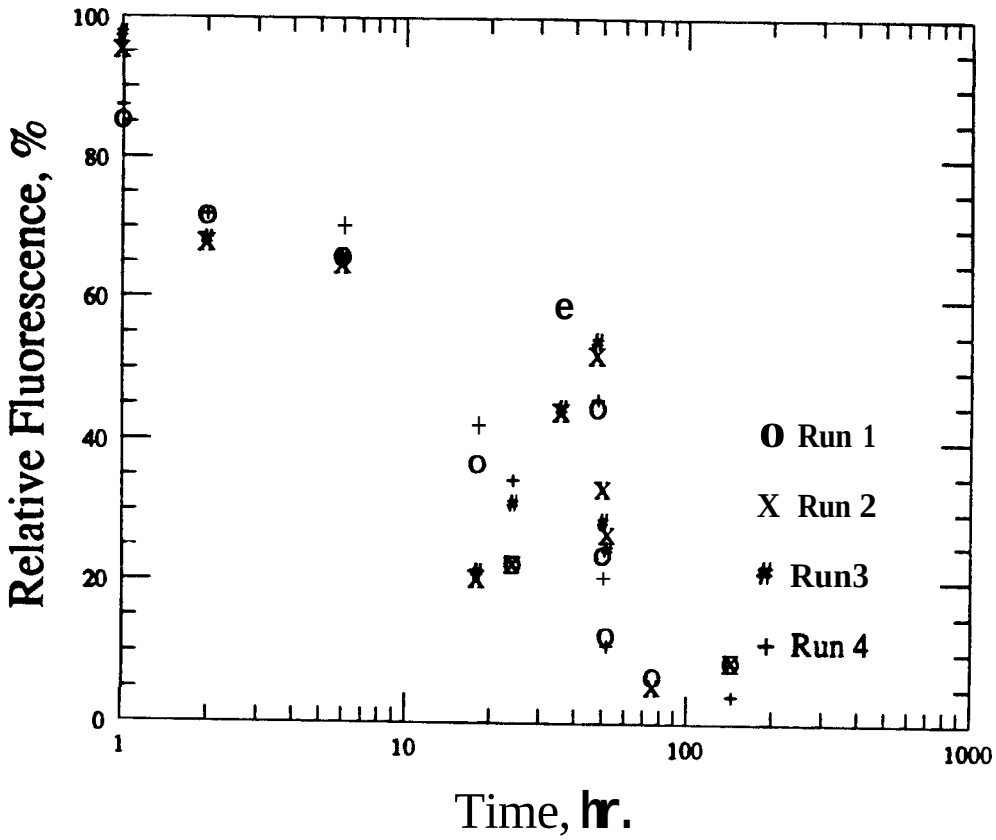

Figure 5: Relative Fluorescence vs. Time for Rhodamine WT (200 ppb) at 200°C.

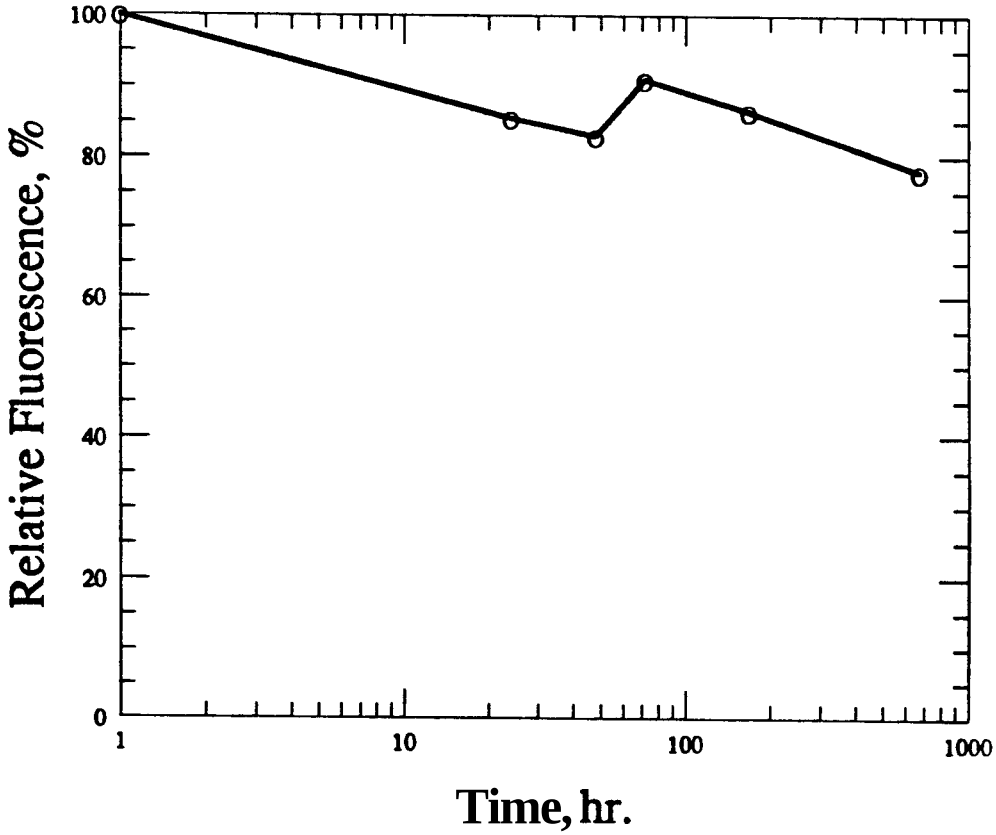

Figure 6: Average Relative Fluorescence vs. Time for Rhodamine WT (200 ppb) at 100°C from four runs.

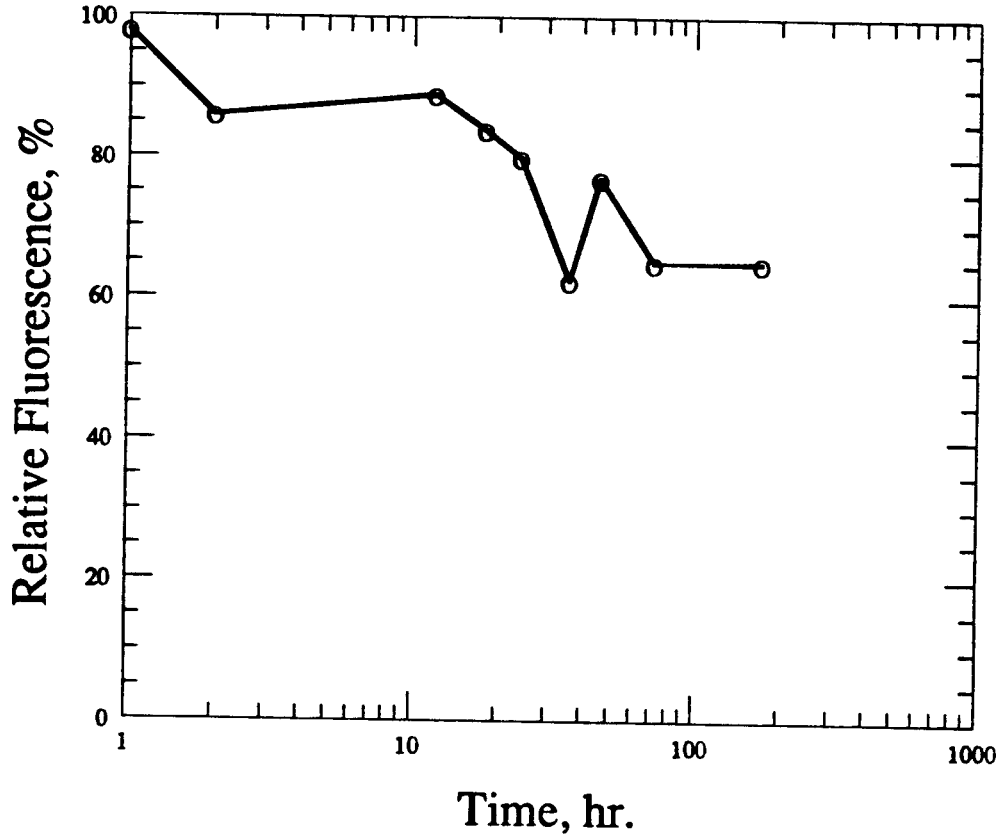

Figure 7: Average Relative Fluorescence vs. Time for Rhodamine WT at 150°C from four runs.

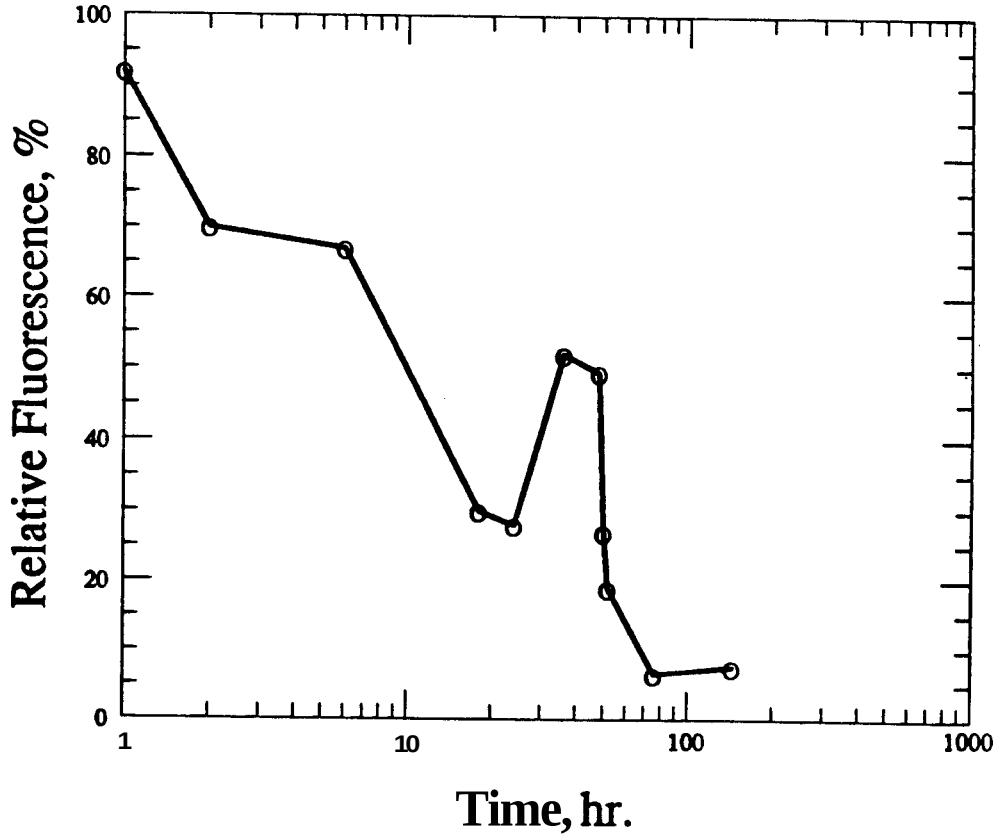

Figure 8: Average Relative Fluorescence vs. Time for Rhodamine WT at 100°C from four runs.

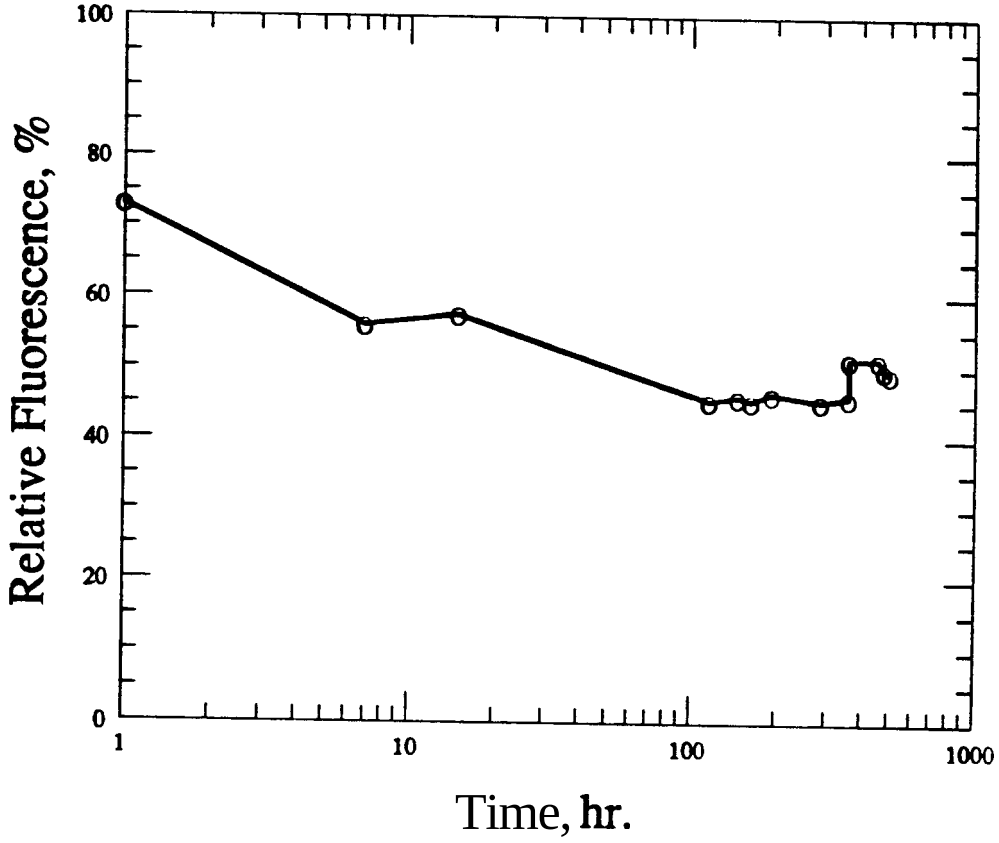

Figure 9: Relative Fluorescence vs. Time for Fluorescein (50 ppm) at 100°C.

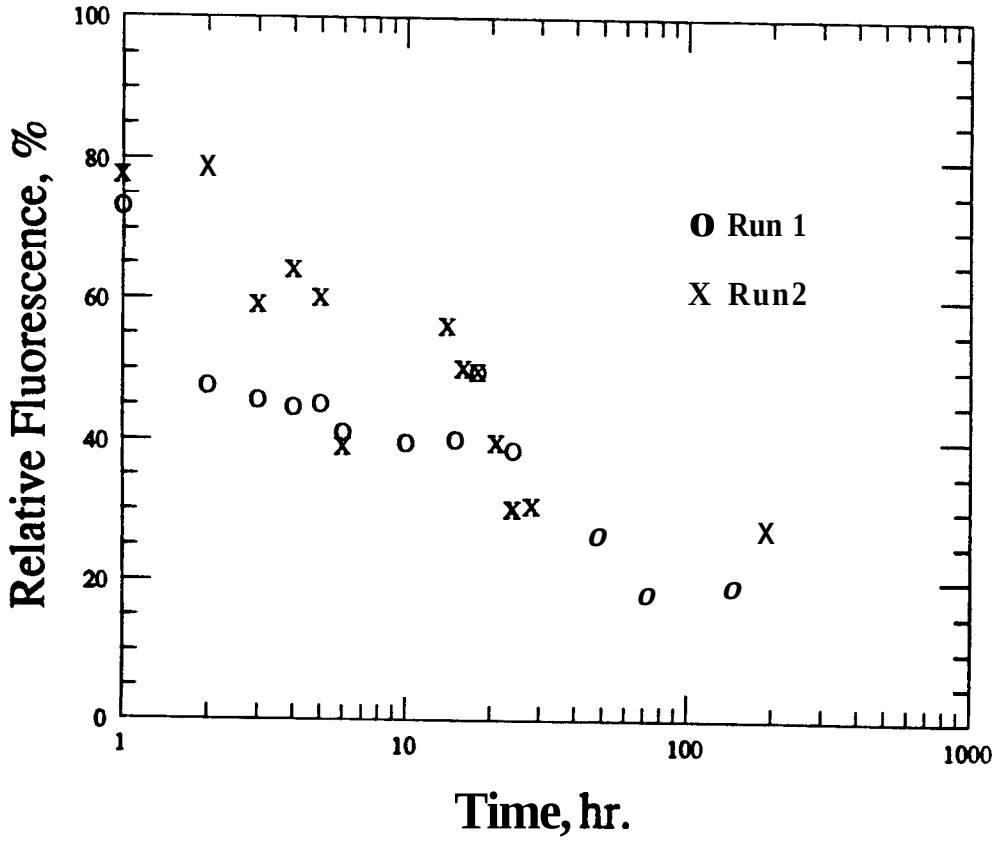

Figure 10: Relative Fluorescence vs. Time for Fluorescein (50 ppm) at 150°C.

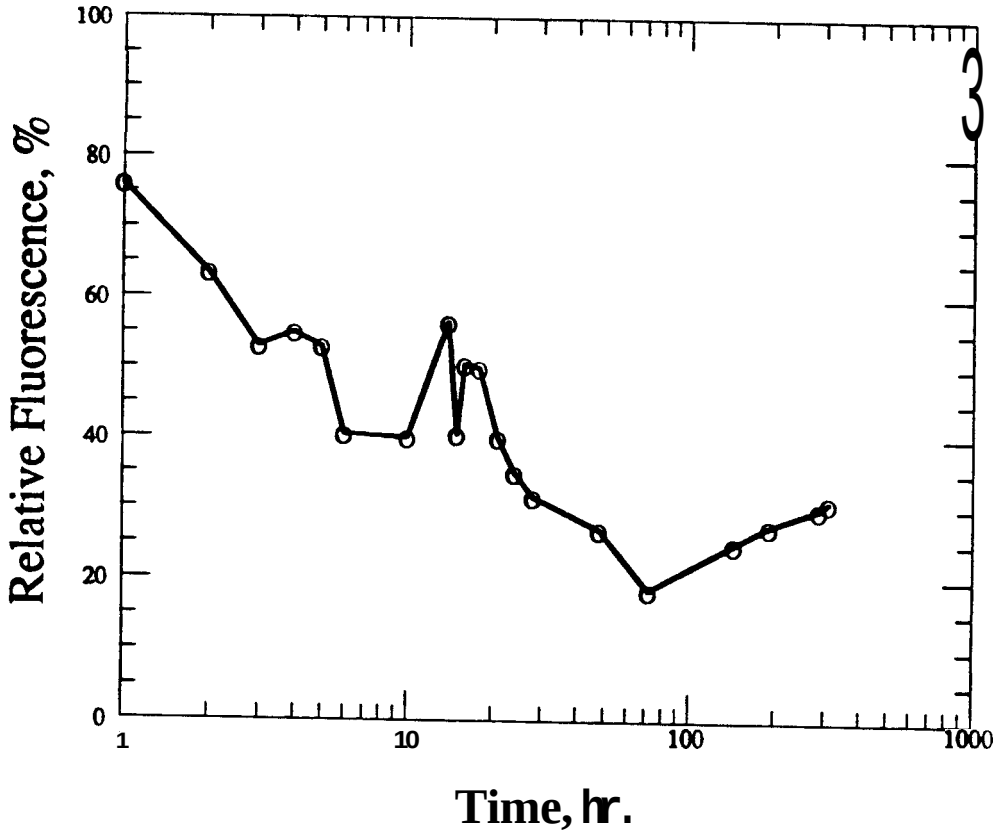

Figure 11: Average Relative Fluorescence vs. Time for Fluorescein (50 ppm) at 150°C from two runs.

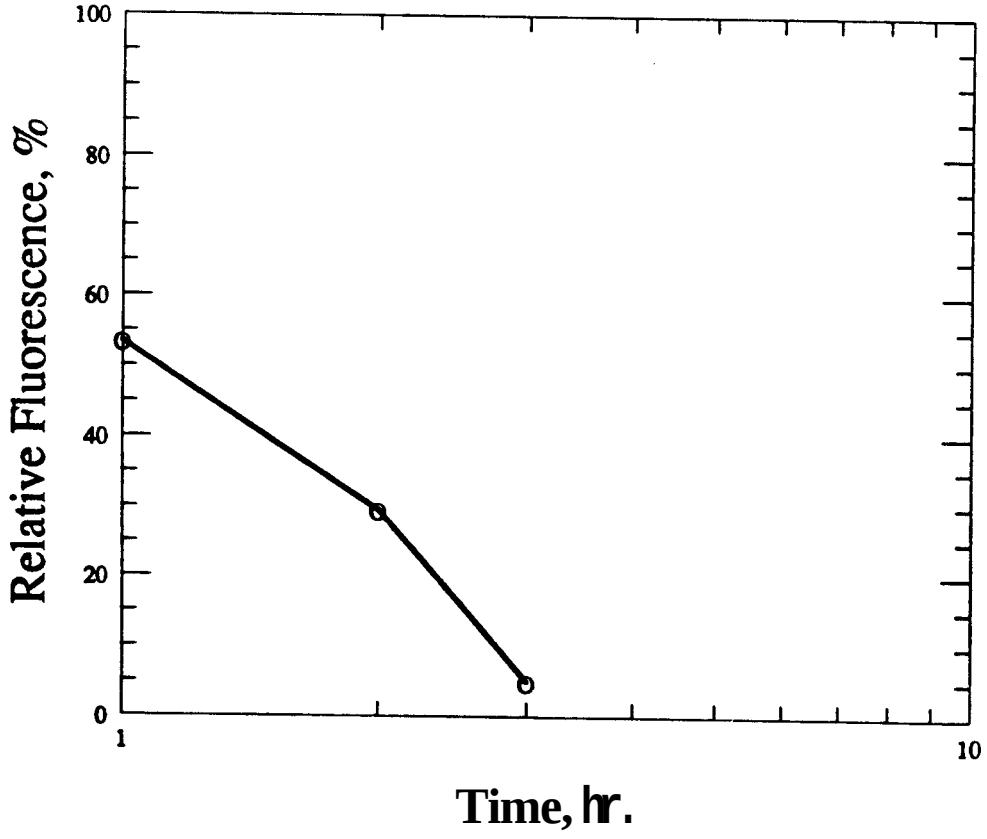

Figure 12: Relative Fluorescence vs. Time

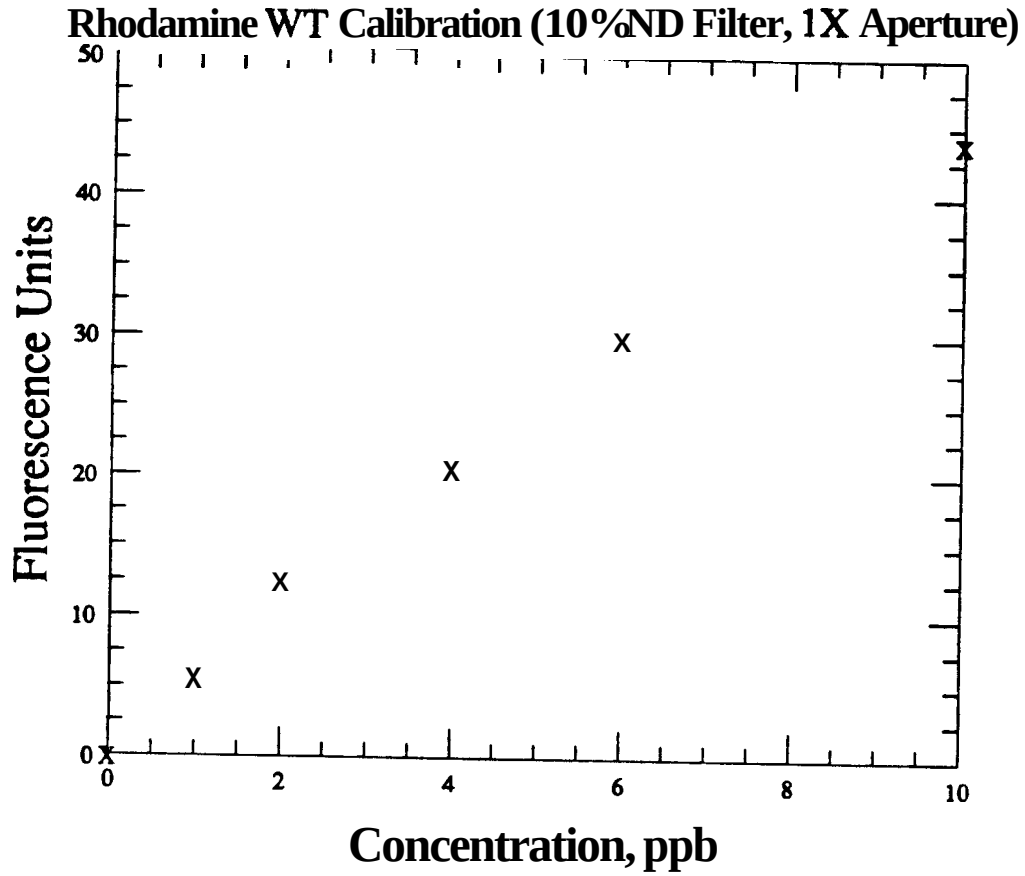

Figure 13: Relative Fluorescence vs. Concentration for Rhodamine WT (1-10 ppb) at 25°C.

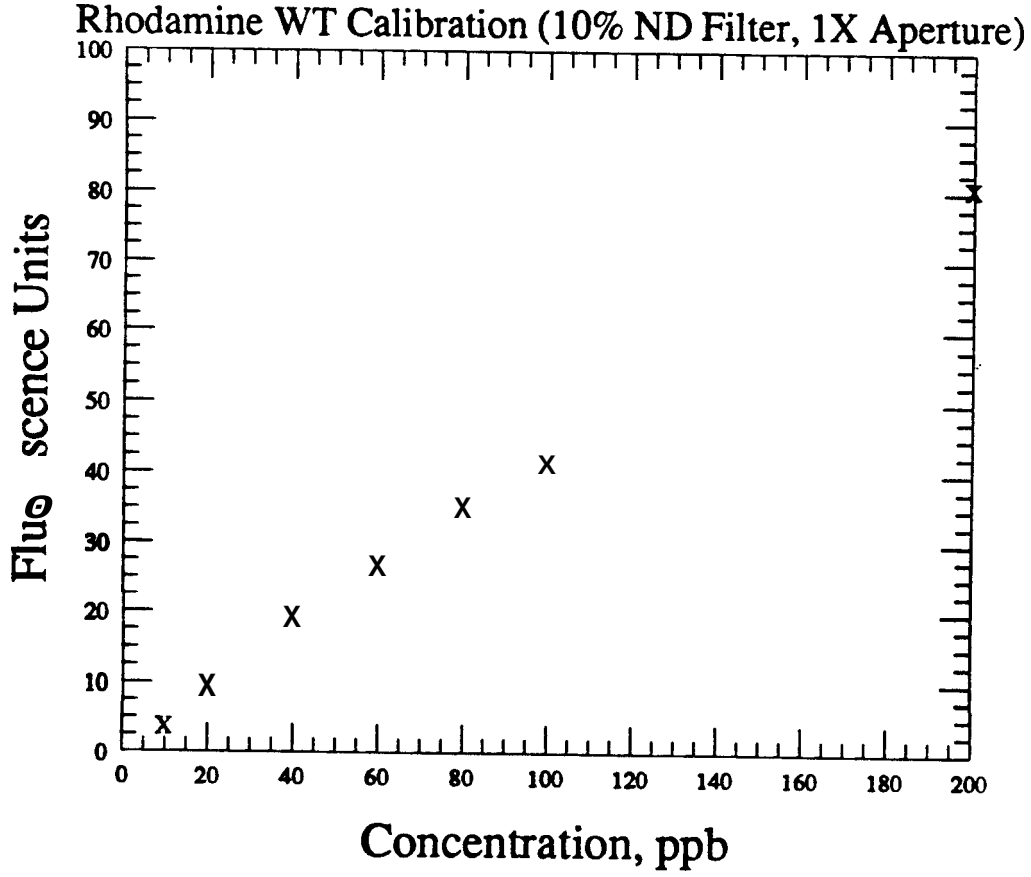

Figure 14: Relative Fluorescence vs. Concentration for Rhodamine WT (10-100 ppb) at 25°C.

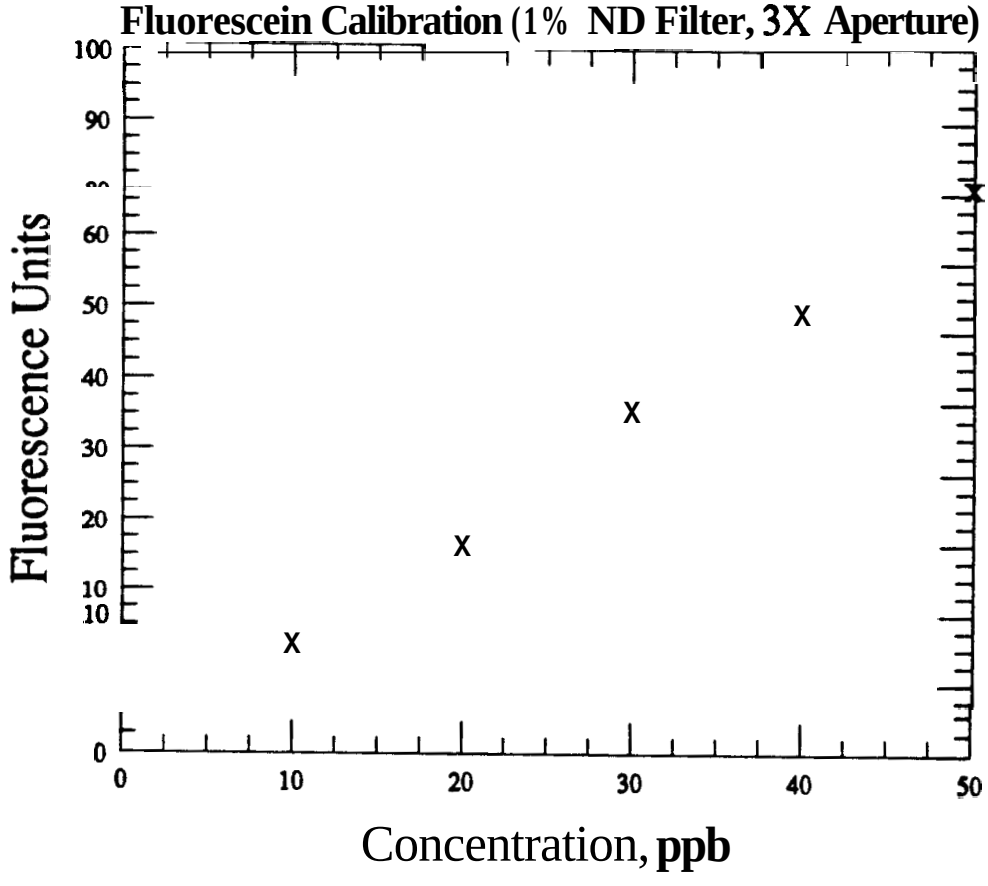

Figure 15: Relative Fluorescence vs. Concentration for Fluorescein (10-50 ppm) at 25°C.

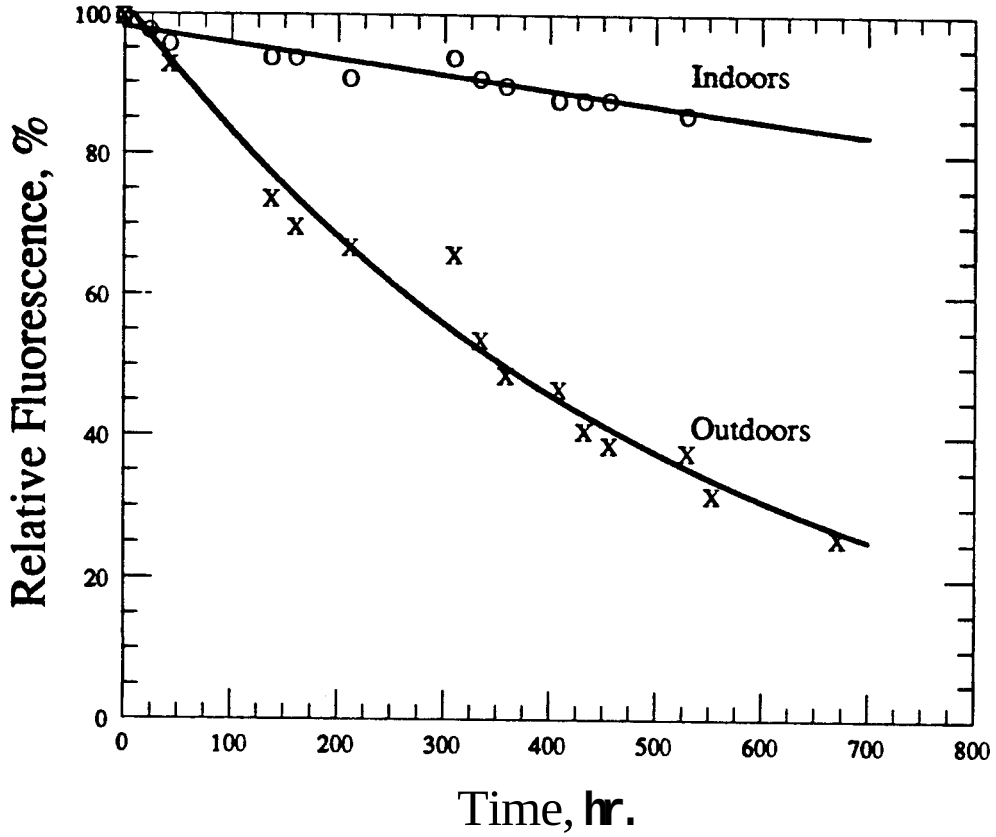

Figure 16a: Photochemical Decay for Rhodamine WT (200 ppb).

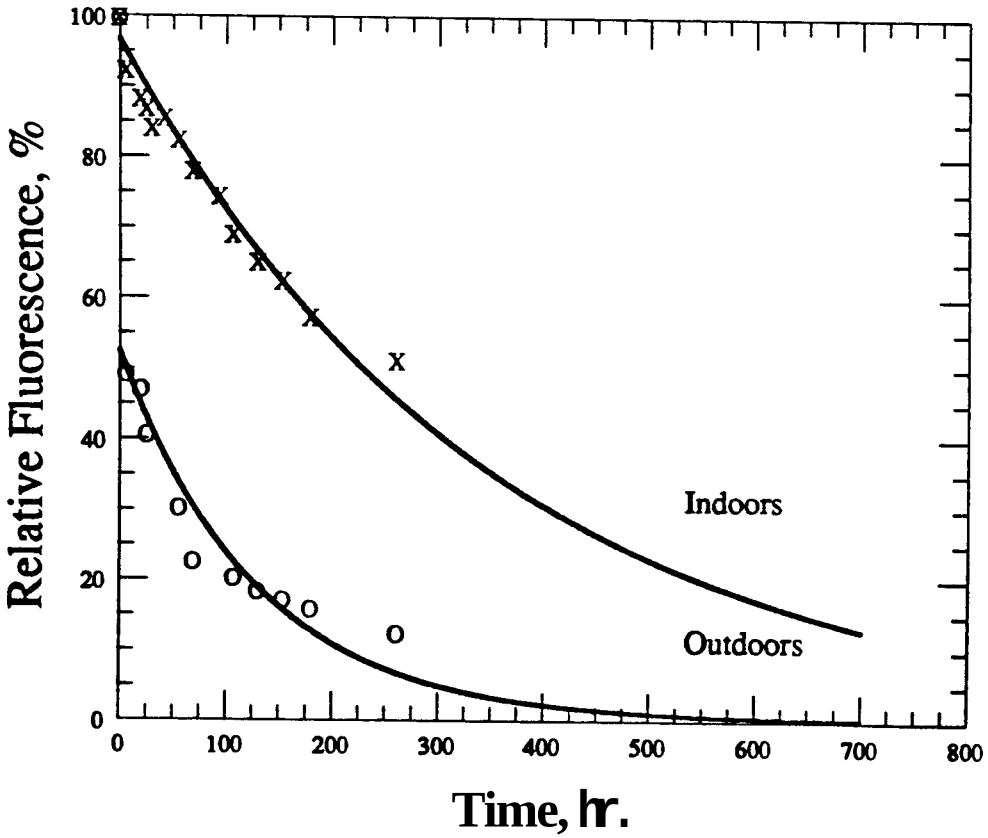

Figure 16b: Photochemical Decay for Fluorescein *(50* ppm).

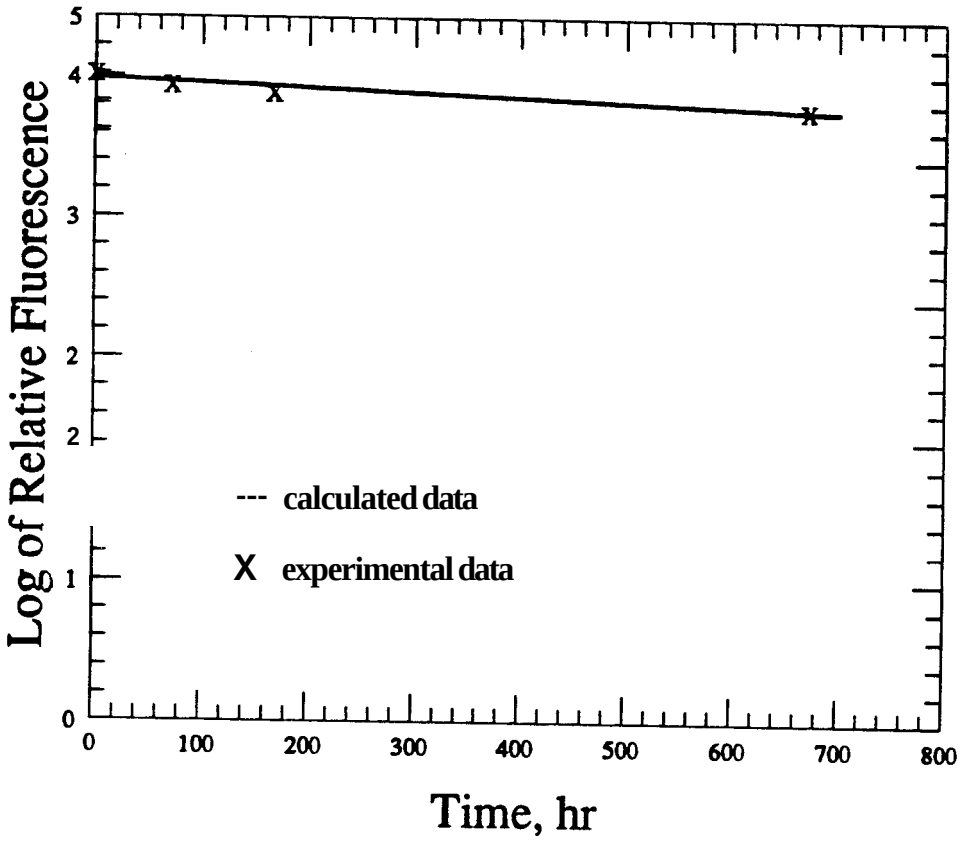

Figure 17: Log of Relative Fluorescence Versus Time for Rhodamine WT at 100°C.

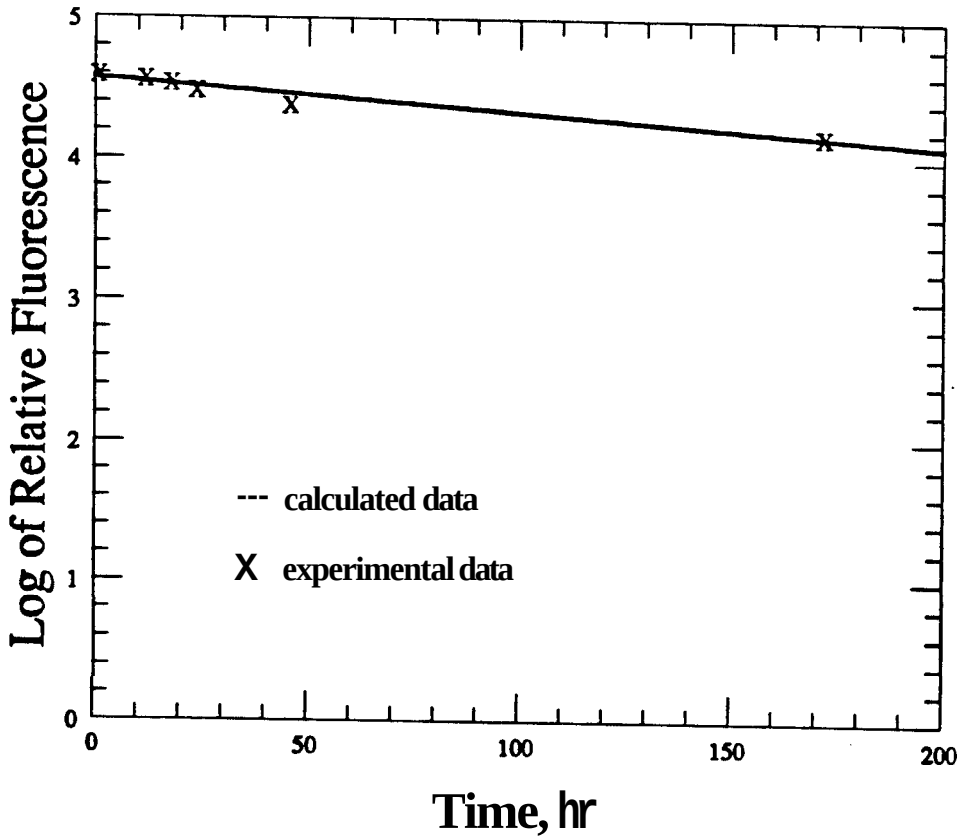

Figure 18: Log of Relative Fluorescence Versus Time far Rhodamine WT at 150°C.

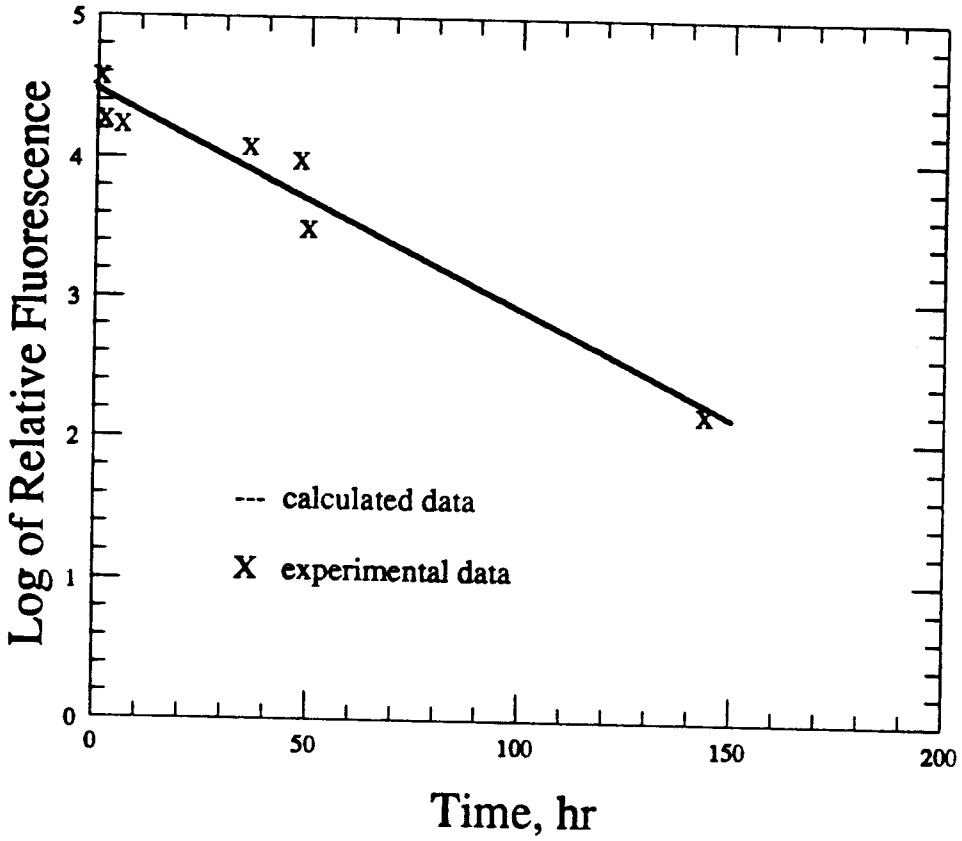

Figure 19: Log of Relative Fluorescence Versus Time for Rhodamine WT at 200°C.

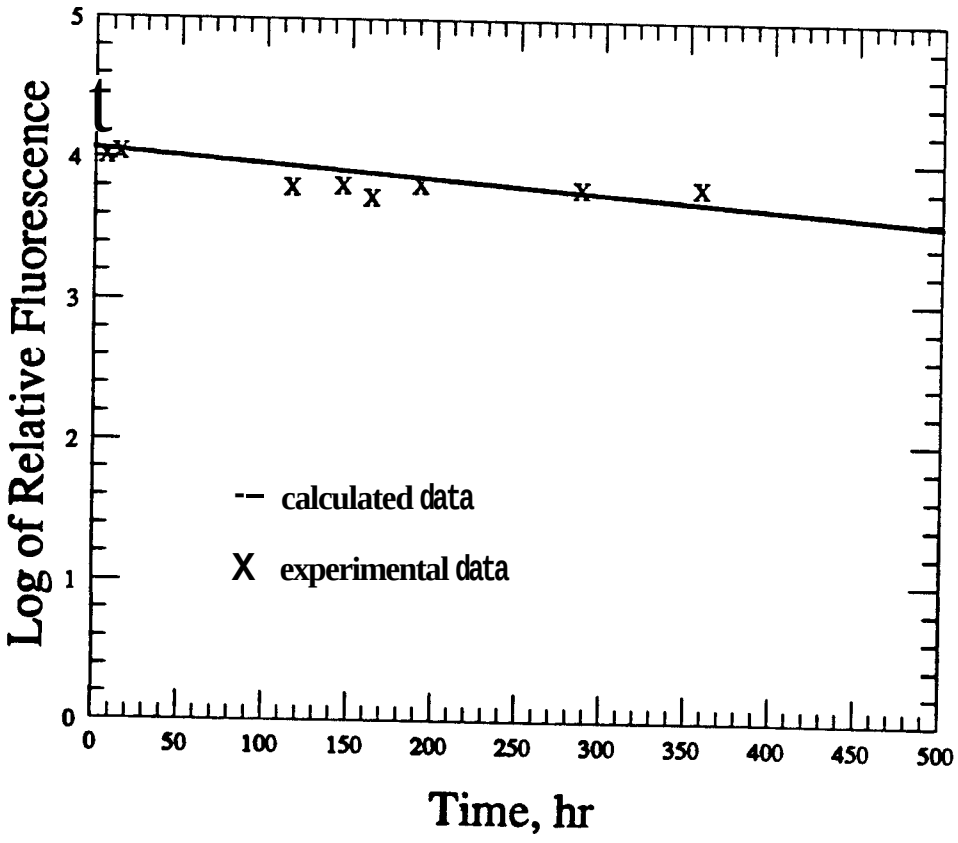

Figure 20 Log of Relative Fluorescence Versus Time for Fluorescein at 100°C.

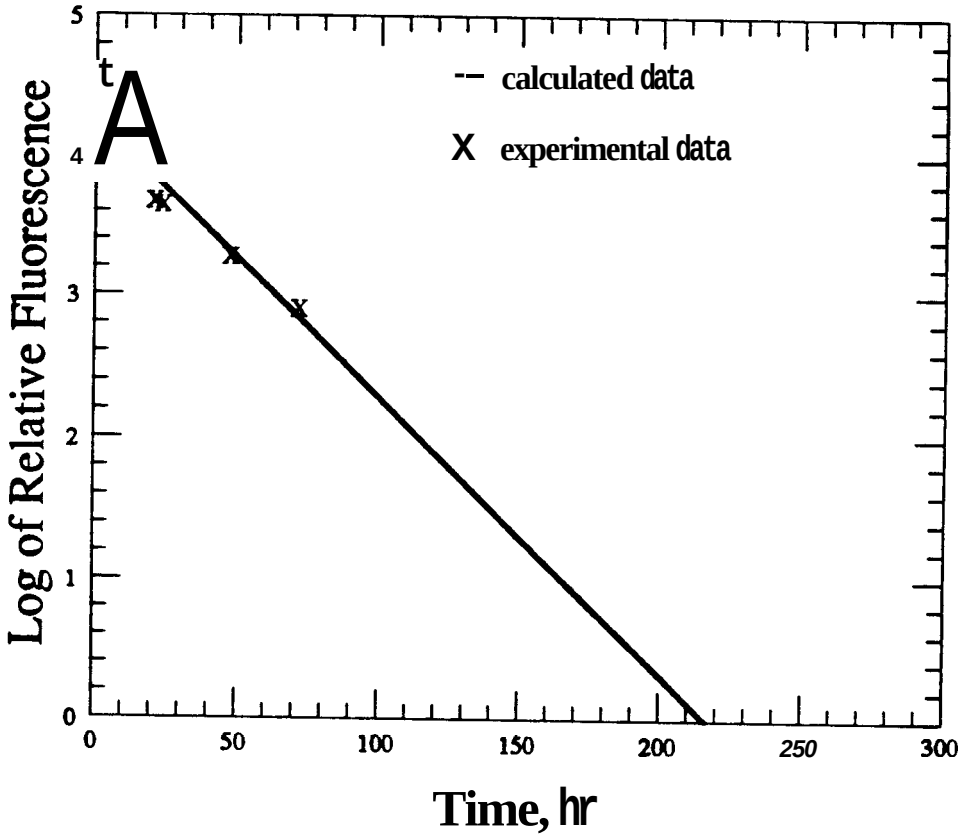

Figure 21: Log of Relative Fluorescence Versus Time for Fluorescein at 150°C.

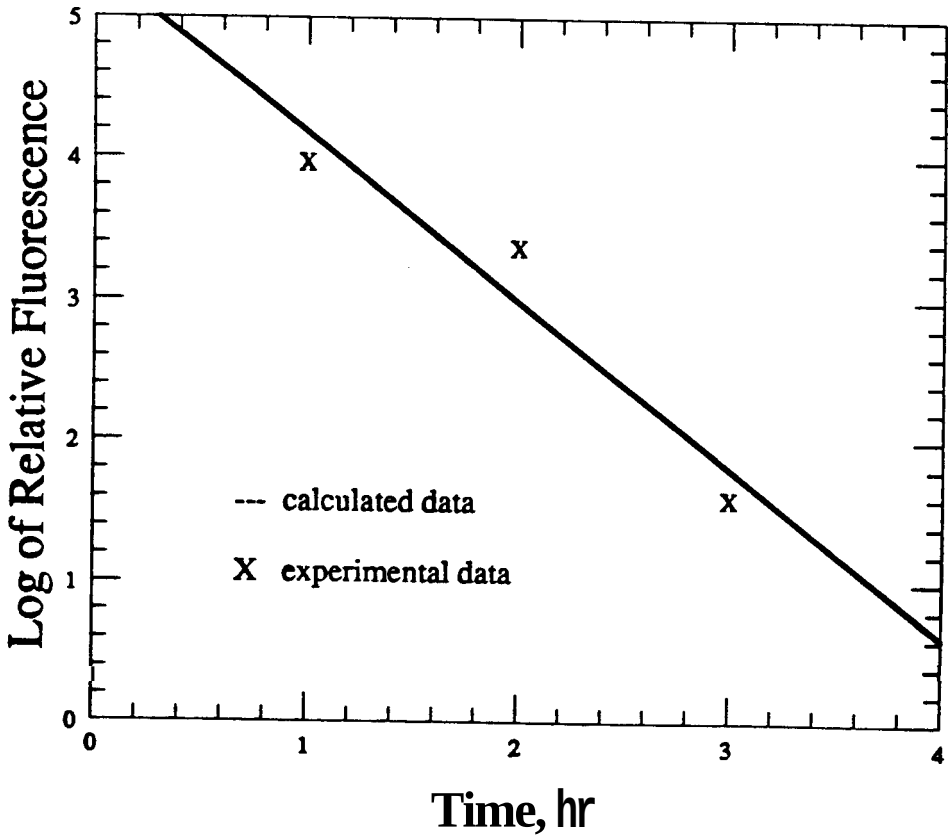

Figure 22: Log of Relative Fluorescence Versus Time for Fluorescein at 200°C.

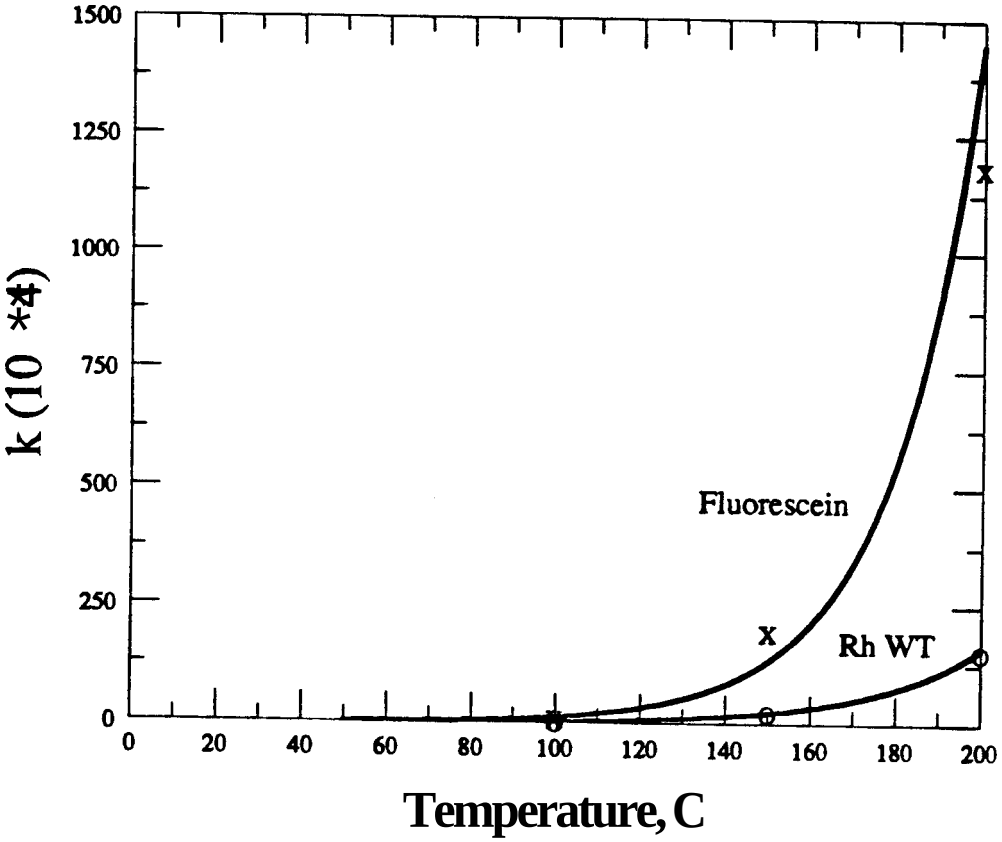

Figure 23: Rate Constants Vs. Temperature for Rhodamine WT and Fluorescein.

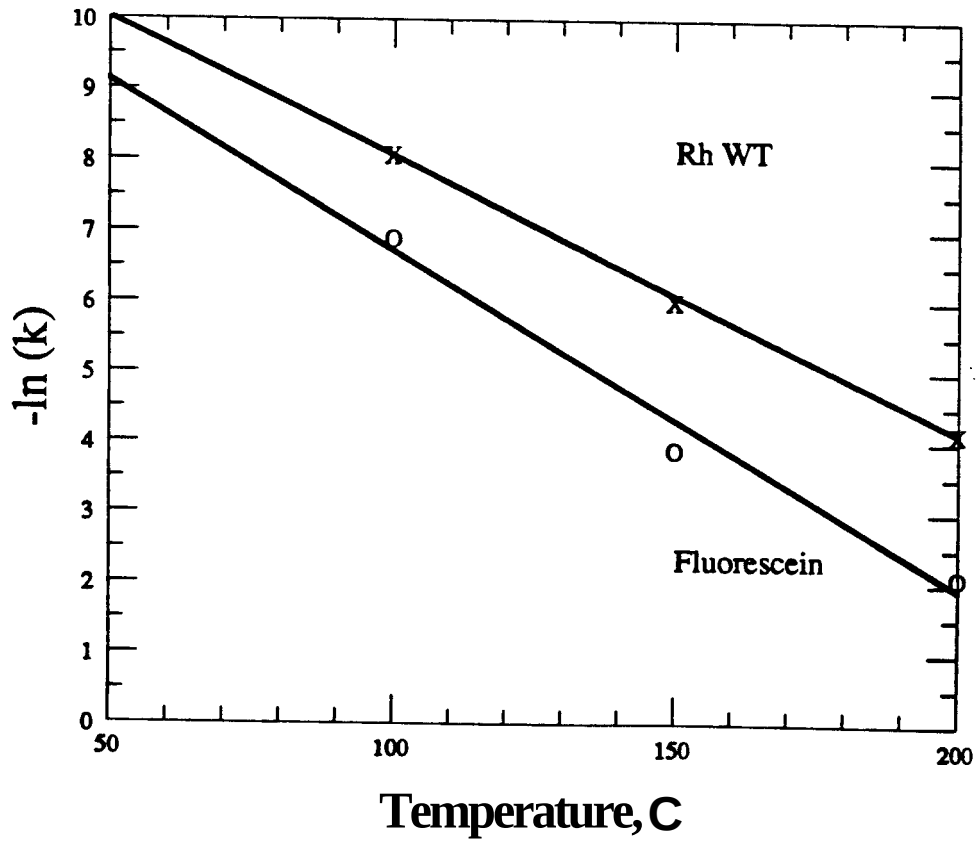

Figure 24: Log of Rate Constants Vs. Temperature for Rhodamine WT and Fluorescein.

APPENDIX A

Reaction Rate Calculations

If a dye A changes to species *B:*

$$A \longrightarrow B \tag{A1}$$

then the rate R of this reaction is given by:

$$R = -\frac{d[C]}{dt} \tag{A2}$$

where the square brackets indicate concentration of the dye. Decomposition reactions of first order (R is proportional to concentration) are given by:

$$\frac{d[C]}{dt} = -k[C] \tag{A3}$$

where k is the rate constant. Fluorescence is related to concentration (see calibration curves for Rhodamine WT and Fluorescein, Figures 13 through 15). Replacing C with F in equation (A3) and integrating :

$$\ln \frac{[F]}{[F_0]} = -kt \tag{A4}$$

$$\frac{[F]}{[F_0]} = Ae^{-kt} \tag{A5}$$

where $[F_0]$ is fluorescence at $t = 0$, A is a scaling factor and $[F]$ is fluorescence at $t = t$. So for a given temperature at various time intervals, the value of k can be determined from a graph of $\ln [F]$ against time. In this way a suite of k values can be experimentally generated. Table 1A summarizes the data for *Equation* AS. The last column of Table 1A contains correlation coefficient values, R, which indicate how well the data fitted *Equation* AS. R of 1.00 is a perfect fit; R equals to zero is no fit. The scaling factors and first-order rate constants for

rhodamine WT are correlated with temperature in Appendix B to give a useful relation (see Appendix B).

APPENDIX B

Data Correlation

The scaling factors and first-order rate constants of Rhodamine WT shown in Table 1A were correlated with temperature. Graphs of *ln A Vs. Temperature* and *ln B Vs. Temperature* were found to be linear:

$$A = a_1 e^{-b_1 T} \tag{B1}$$

$$k = a_2 e^{b_2 T} \tag{B2}$$

where a_1 and a_2 are scaling factors, and b_1 and b_2 are exponential factors. Table 1B lists the values of a_1, a_2, b_1 and b_2 for Rhodamine WT. *Equations B1* and *B2* can be substituted in *Equation A5* of *Appendix A* to give a general correlating formula for relative fluorescence (%) for Rhodamine WT as a function of time, t hours and temperature, T °C:

$$\frac{[F]}{[F_0]} = a_1 e^{-(b_1 T + (a_2/b_2) e^{b_2 T})} \tag{B3}$$

Equation B3 can be used to estimate the reduction of fluorescence of Rhodamine WT at a given reservoir temperature if the residence time is known. The scaling factors and first-order rate constants for fluorescein did not correlate well with temperature.