

### 5.3 Photodegradation

To measure the effects of heat and sunlight four different fluorescein solutions (A to D) were kept in the dark at room temperature, kept in the dark at more than 60°C, or exposed to bright sunlight, and the absorbance was monitored frequently throughout the test period. The average change in absorbance for solutions A (pH 11.2), B (pH 5.2) and C (pH 11.2 + Na<sub>2</sub>S) is shown in Figure 9. Solution D (pH 5.2 + Na<sub>2</sub>S) results are not shown because a precipitate formed during the test and interfered with the absorbance readings. The data from this test are listed in Appendix F.

Figure 9 shows that the heated and room temperature fluorescein controls were stable throughout the two-hour test period. The stability of these solutions compared with the instability of the sunlight exposed solutions shows that it is more important to protect a fluorescein solution from bright light than from heat. The stability of these controls confirms the observations of Diehl and Horchak-Morris (1987) and Lindqvist (1960) that fluorescein solutions are stable if kept in the dark but contradicts the observation of Leonhardt *et al.* (1971) that hot aqueous fluorescein solutions are unstable.

Solutions exposed to sunlight showed a rapid absorbance decrease (Figure 9). The average absorbance reduction for the two-hour exposure was 98% for solution A, 57% for Solution B and 20% for solution C. This confirms that fluorescein degrades quickly in bright sunlight and corroborates the observations made Feuerstein and Selleck (1963) and Smart and Laidlaw (1977). The addition of a small quantity of sodium sulphide greatly reduced the rate of absorbance decline (Solution C) compared to the same solution without sodium sulphide (Solution A), and the pH 5.2 solution (Solution B) showed less photodegradation than the pH 11.2 solution (Solution A). This indicates that the photodegradation rate is not solely dependent on the light intensity and that both pH and water chemistry influence the degradation rate.

If the natural log of the normalised absorbance is plotted against time the degradation rate constants can be compared. Gradients of sun-exposed solutions are shown in Figure 10 along with the R<sup>2</sup> values. The different rate constants of -1.96, -0.47 and -0.10 hour<sup>-1</sup> for solutions A, B and C confirm that the solution composition has a substantial impact on the

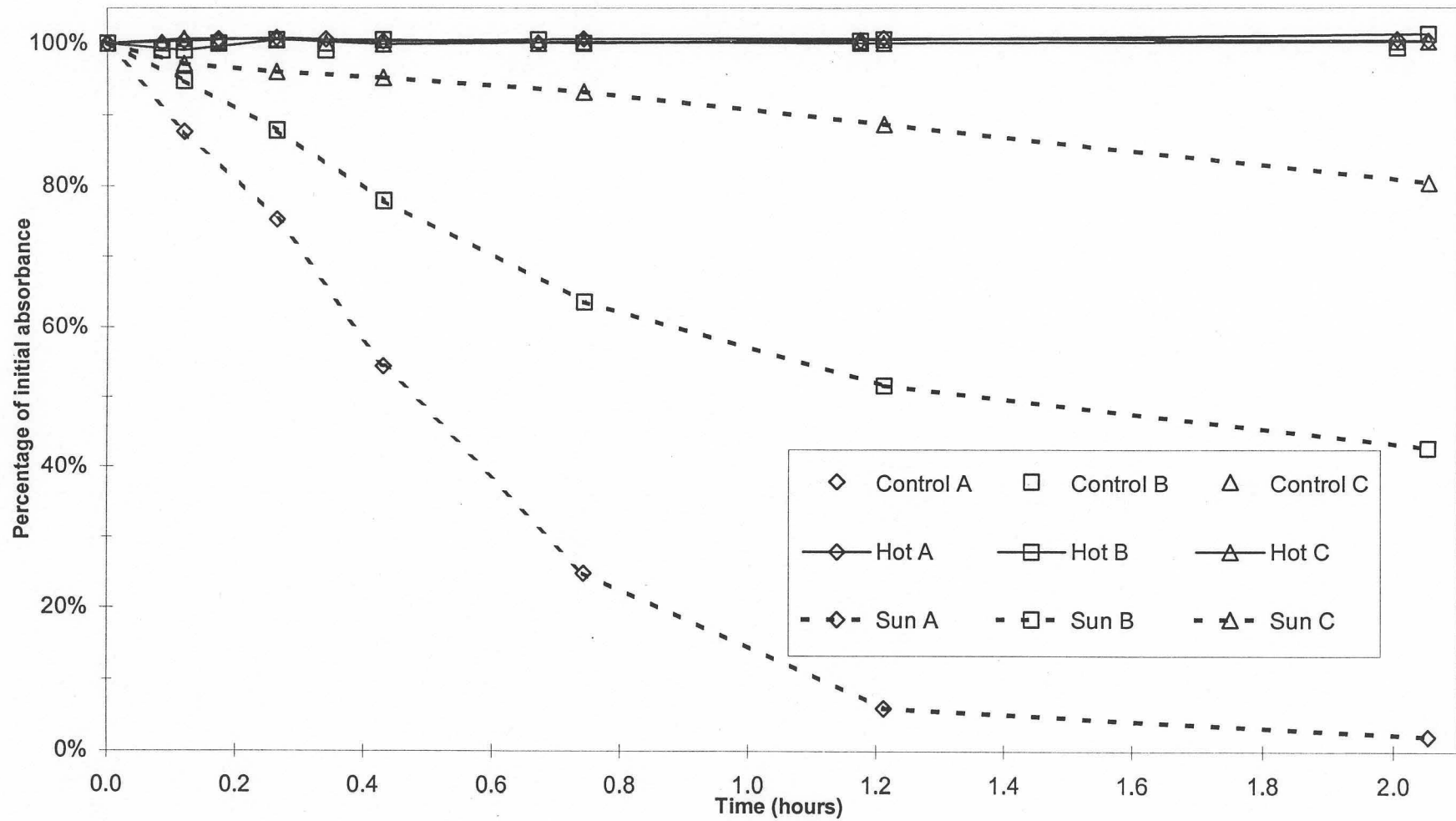


Figure 9 Comparative effects of sunlight and heat on buffered fluorescein solutions. A = pH 11.2, B = pH 5.2 and C = pH 11.2 + Na<sub>2</sub>S.

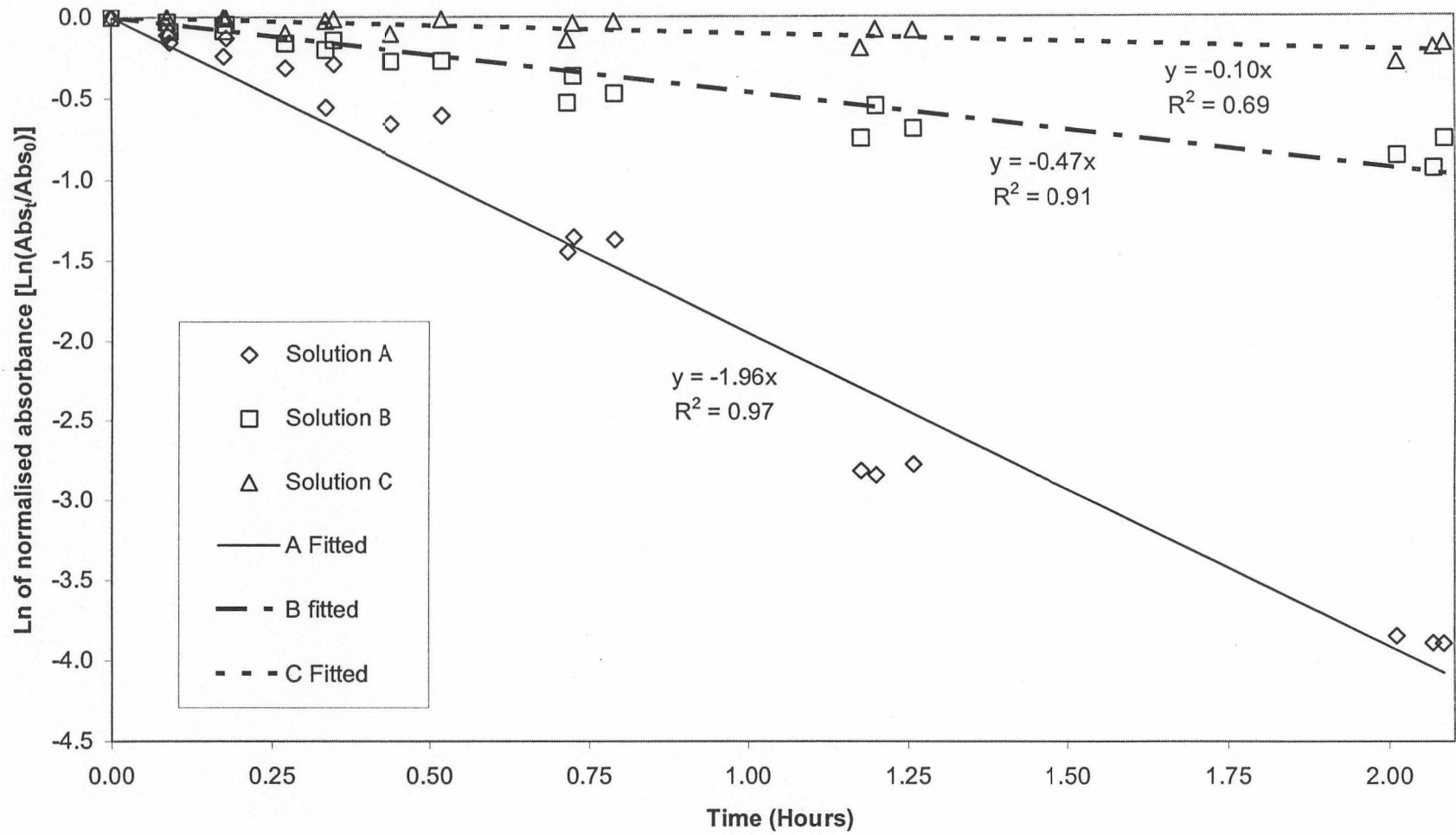


Figure 10 Degradation rates of buffered fluorescein solutions exposed to sunlight. A = pH 11.2, B = pH 5.2 and C = pH 11.2 + Na<sub>2</sub>S.





photodegradation rate. A  $-0.256 \text{ hour}^{-1}$  photodegradation coefficient for fluorescein has been reported for a three-day period of bright sunlight however the nighttime hours were included in this calculation (Feuerstein and Selleck, 1963). This  $-0.256 \text{ hour}^{-1}$  decay coefficient is almost eight times lower than the  $-1.96 \text{ hour}^{-1}$  rate constant found in this study so this difference cannot be explained simply by assuming that the nighttime period halved the light exposure. One reason for this difference is that Feuerstein and Selleck (1963) used distilled water rather than the buffered high pH solution used in this experiment so although their solution pH was not reported it might be expected to be closer to neutrality. This explanation appears correct because the solution B (pH 5.2) photodegradation rate was  $-0.47 \text{ hour}^{-1}$ , which is close to the doubled  $-0.256 \text{ hour}^{-1}$  value.

The  $R^2$  values for solutions A and B are acceptable at 0.97 and 0.91, while C is much lower at 0.69 (indicated on Figure 10). This lower correlation value was due to the influence of a single test run, and if that data set is excluded from all calculations A to C, the  $R^2$  values would all be greater than 0.93.

The practical implications of this experiment are that while reducing the pH and adding sodium sulphide might improve the absorbance stability of fluorescein samples, these benefits are not as important as protecting the solution from bright light. Further, the results show that it will not be possible to accurately compensate for the effects of light exposure unless the other rate influencing variables have been quantified.

The high photodegradation rate of fluorescein does appear to compromise its use as a tracer but this same characteristic would make it especially useful in situations where a more visibly persistent tracer would be undesirable, e.g. provoking public concern. However this photolabile nature should not be a problem for tracer studies performed inside reactor vessels or at night.

## 5.4 Fluorescein recovery in elution trials

### 5.4.1 Fluorescein measurement method evaluation

This experiment uses the  $pK_a$  data and absorptivity factors reported in Section 5.1 to determine how much fluorescein is recovered during column elution tests, and compares this detection method with a simpler fluorescein detection method (KOH addition). Figure 11 shows how the absorbance of the elution samples changed after adding a small quantity of KOH powder to increase the pH above 10. This strong linear relationship ( $R^2 > 0.997$ ) made it possible to convert the experimental absorbance readings (pre-KOH addition) to their post-KOH equivalents using the simple formulas shown next to each “pH Fit” on Figure 11. This means that complex calculations can be avoided if the sample pH is increased before its absorbance is tested. This observation is similar to the recommendations of Smart and Laidlaw (1977) to either perform a pH adjustment before measuring the tracer concentration, or to perform the tracer calibration using the water under study.

The sensor elution data (Appendix G) were converted to absorbance values, corrected for stray-light effects and then converted to fluorescein concentrations. A typical elution profile is shown in Figure 12 where the fluorescein concentration is plotted against flow. The flow units have been standardized such that 1 theta unit is equal to the water volume within the gravel column. Figure 12 shows that it makes little difference whether the fluorescein concentration is calculated from the absorbance value using the activity corrected  $pK_a$ s and the pH, or whether the sample pH is increased before measuring the absorbance. The percentage of fluorescein recovered by these two methods for all 28 tests are shown in Table 9. These data demonstrate that the calculation method and KOH addition method have practically identical effects, with less than 1.2 % difference between the average percentage recoveries for each pH run (A – B Avgs).

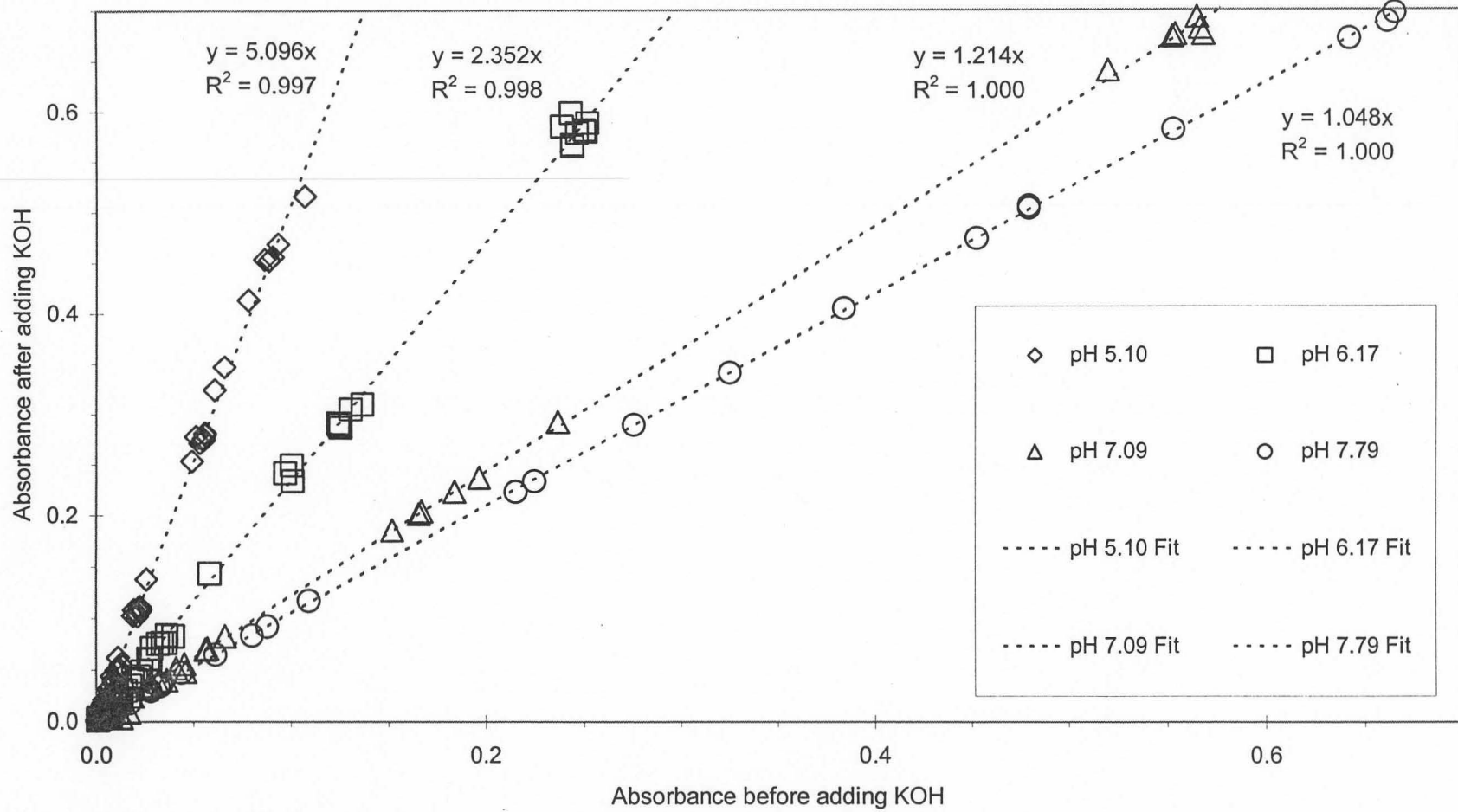


Figure 11 Absorbance change produced by increasing the sample pH (adding KOH)

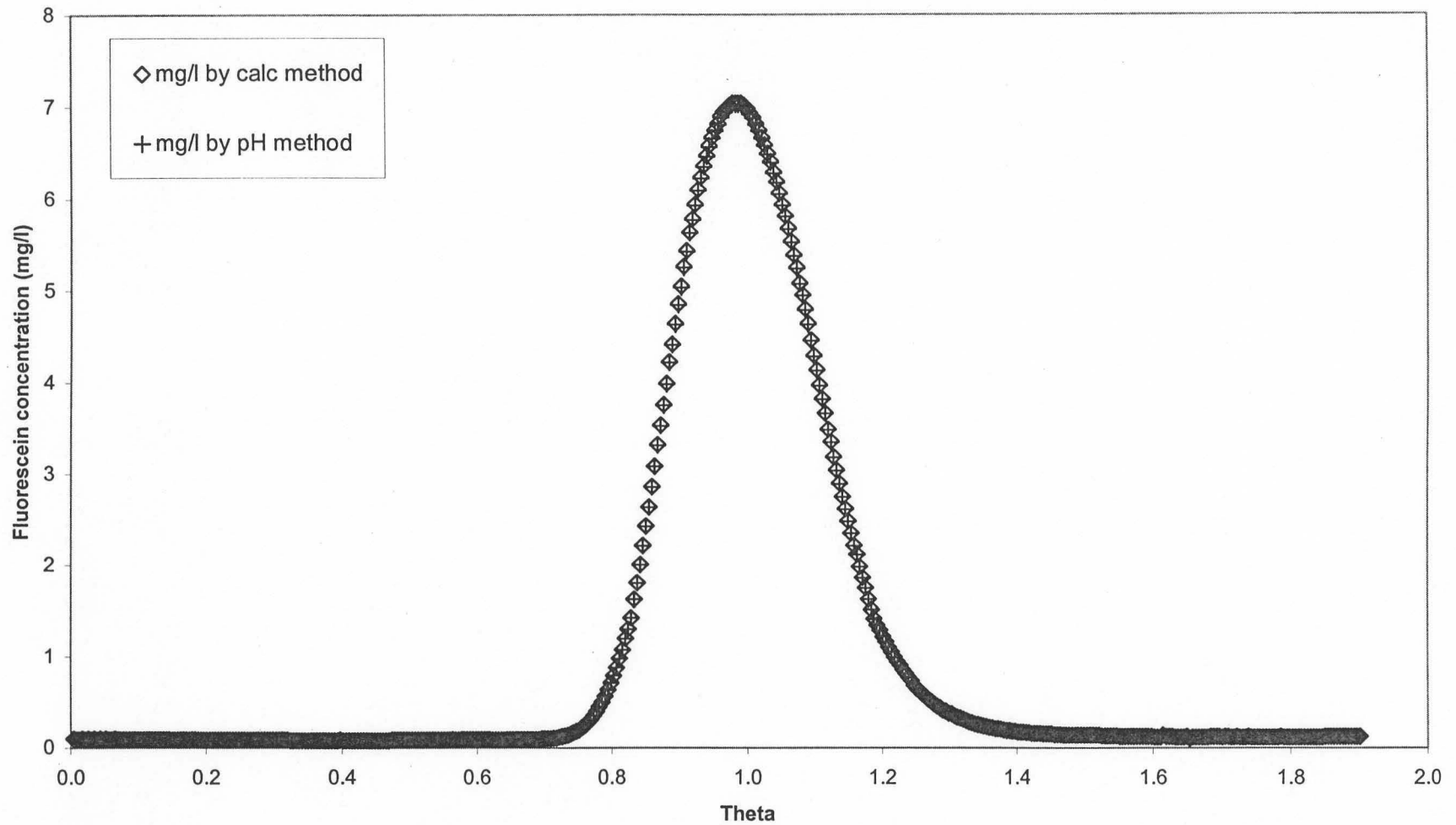


Figure 12 A typical elution profile showing the calculation and pH adjustment method results



**Table 9 Comparison of fluorescein recoveries**

Percentage recovery using calculation method											
Run	1	2	3	4	5	6	7	8	Avg. (A)	Std Dev.	
pH 5.1	94	91	95	104	101	105	110	113	101.6	7.8	
pH 6.2	87	87	96	104	103	99	105	105	98.4	7.7	
pH 7.1	92	98	105	104	109	114			103.9	7.7	
pH 7.8	94	98	90	93	88	91			92.3	3.5	
Percentage recovery using KOH addition method											
Run	1	2	3	4	5	6	7	8	Avg. (B)	Std Dev.	A - B (Avs)
pH 5.1	95	91	95	105	103	107	112	115	102.8	8.6	-1.2
pH 6.2	85	85	97	104	104	99	105	107	98.3	8.8	0.1
pH 7.1	92	99	105	104	109	114			103.8	7.7	0.2
pH 7.8	94	99	91	94	88	91			92.8	3.6	-0.5

#### 5.4.2 Fluorescein recovery

Fluorescein is generally not recommended as a quantitative tracer (Feuerstein and Selleck, 1963, Smart and Laidlaw, 1977 and Wilson *et al.*, 1986) and no comparative elution trial data were found. However, some sediment adsorption data (Smart and Laidlaw, 1977) suggest that 98% of fluorescein should be recoverable from 2g/l suspensions of mineral sediments. Unfortunately this adsorption figure does not correspond with the graphical data presented by these researchers so it will not be possible to use this 98% recovery as a guideline value. The fluorescein recoveries from this study are shown in Table 9 as a percentage of the injected quantity.

If the tracer sensor and spectrophotometer readings have been correlated correctly and the absorbance/concentration determination methods are correct, then it would be reasonable to expect average recoveries of 100 %. Although the pH 5.1, pH 6.2 and pH 7.2 trials show average recoveries close to 100%, the pH 7.8 trials show an average recovery of 92.5%. There are at least two reasons for this lower recovery:

- While the sensor and spectrophotometer readings do correlate quite well within the experimental concentration range, fluorescein does not conform to Beer's law in this spectrophotometer. This Beer's law deviation underestimates the fluorescein





concentration and becomes more pronounced as the absorbance increases so the highest and sharpest elution peaks of the high pH trials will be most likely to show reduced recoveries.

- The tracer sensor used in these tests is an experimental device and may be sensitive to unrecognised variables. This sensor was the third constructed during this investigation. Earlier designs suffered from changes in absorbance as the sensor construction materials deformed, transparent plastics whitened (on prolonged water contact), construction glues became opaque, and the light-dependent resistor corroded. These problems had been eliminated in the third design.

While recognising these potential inaccuracies, the average fluorescein recovery in these trials was 99.4%, showing that fluorescein did behave conservatively. In future tracer studies it will be vital to identify the cause of any deviation from complete recovery as this investigation demonstrates that conservative behaviour of fluorescein is possible if one correctly evaluates the system parameters.

This study further demonstrates that in addition to the absorbance behaviour the transport behaviour of fluorescein also changes with pH and this is exactly what would be expected (Behrens, 1986). As the fluorescein ionic species become less negatively charged when the pH decreases, they become less soluble and more prone to adsorption on the gravel. This manifests as a change in elution profile that is clearly visible in the retarded profile of the pH 5.12 run overlaid on the pH 7.79 run shown in Figure 13. This can also be seen in the standard deviations of the lower pH trials, which are twice as high as the pH 7.8 trial. The pH 7.8 trial standard deviation is lower because the fluorescein is present as the more soluble dianion and is thus less likely to adsorb onto the column gravel surfaces and interfere with the subsequent test run.

Other than their detectability, there is no reason to expect that tracers behave differently from compounds that have similar molecular structures. So while a susceptibility to adsorption might be viewed as a problem, tracers that are susceptible to these phenomena might be better able to identify and quantify these alternative pathways. Once these pathways are better understood it may be possible to alter the system conditions to minimise the spread of a pollutant and/or maximise its decomposition. However, such non-conservative tracers will obviously only be useful if their behaviour is understood in detail.

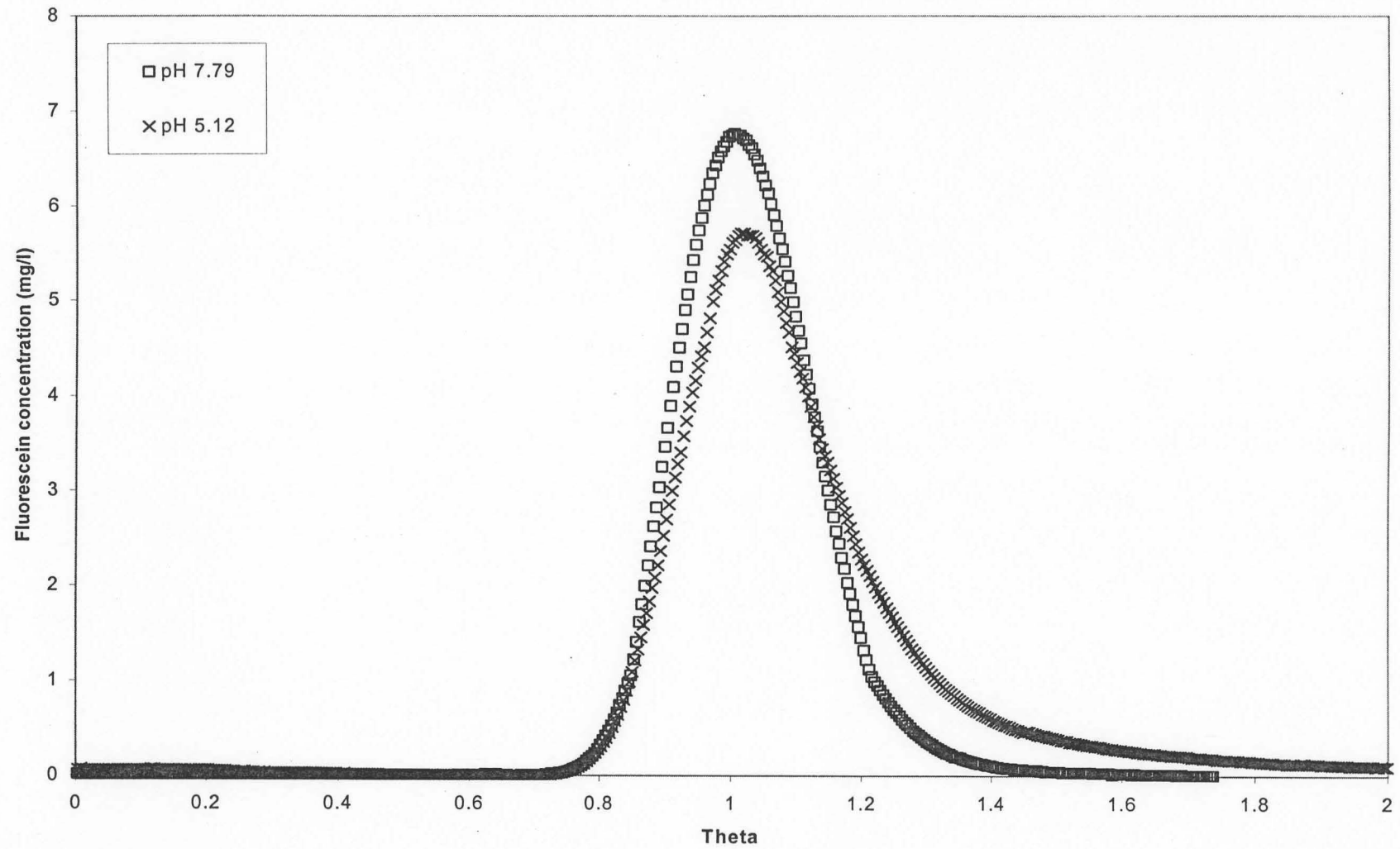


Figure 13 Overlaid elution profiles of two different pH test runs