OPTIMISATION OF THE PHOTOSTIMULATED LUMINESCENCE (PSL) TESTS TO DETECT IRRADIATED DIETARY SUPPLEMENTS

CONTRACT NUMBER A05010

EXPERIMENTAL STUDIES OF PRE-CONCENTRATION, DEPLETION RATE ANALYSIS AND MULTI-WAVELENGTH PSL ANALYSIS

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SUMMARY

This report forms the final deliverable of project A05010 aimed at optimising the photostimulated luminescence (PSL) screening method for dietary supplements. It follows on from the first deliverable which discussed the existing datasets of luminescence measurements, both PSL and TL (thermoluminescence), from a number of surveys of undeclared irradiated foodstuffs including dietary supplements, conducted since 2001. Some 427 samples from official surveys were examined, where both PSL screening and TL analysis had been applied. Of these calibrated PSL data were available from 280 samples. A further 554 analyses from the SUERC archive were also considered where PSL and TL measurements had been made together. These data were used to examine the incidence of all pairs of possible outcomes for PSL screening and TL analysis. 5-8% of positive TL analysis were identified where PSL screening failed to detect material. Similarly, in 9-16% of analyses with negative PSL screening, TL analysis subsequently detected an irradiated component. Calibrated PSL data confirmed that low sensitivity was associated with many of these instances. For these samples, whose very low mineral contents and correspondingly low PSL sensitivities limit the effectiveness of rapid PSL screening, it is possible that pre-concentration of minerals may improve the performance of PSL.

It is clear that there is scope for enhancement of the PSL signal in materials with low sensitivity and also possibly for discriminating between high natural signals of geological origin and recent artificial irradiation. A suite of ten dietary supplement ingredients was used, in both irradiated and unirradiated forms, to assess the performance of two concentration methods; a simple settling through a column of water and a density separation equivalent to one of the steps in the EN1788 TL method for mineral separation.

Initial attempts to enhance the PSL signals by settling minerals in water did not achieved the desired result, so further experiments were undertaken. Two protocols were devised for use with the 10 samples, to compare a one stage settling regime with a two stage settling and density separation, using 10 fold replication. The results show that the 2 stage process achieves higher concentration factors than simple water separation. For both the irradiated and unirradiated samples the mean factor is over 10 compared to 3 fold mean factor for the single stage process. Overall we are able to enhance the PSL signal from these 10 retained materials and although some extracts still prove to be problematic, ethanol dissolution maybe used to aid the signal. Further investigation using other solvents and also other heavy liquids would be beneficial.

Depletion rate analysis and multi-wavelength stimulation were applied to half these samples, those which had passed through the density separation. A further two aliquots of each product were also prepared with the density separation method and stimulated with two different wavelengths. A brief investigation of an alcohol extract was also conducted, with promising results for further study.

Although the concentration factor (PSL signal after pre-concentration divided by initial PSL) varied from product to product, in general the method including the density separation performed better than the simple settling. Further work to assess different settling media and alternative heavy liquids could be undertaken. It was also noted that the irradiated products were "easier" to concentrate than the unirradiated; further work is also needed to explore the reasons for this.

From this initial study, depletion rate analysis over a 300 second measurement can be seen to be a promising tool for distinguishing irradiated and unirradiated materials; again further work on bleached samples and those known to have high natural signals might refine the technique. Suggestions are included for parameters which could be calculated for unknown samples to categorize them. Stimulation with two different wavelengths did not, however, produce as clear-cut a segregation of the two categories of sample,however the use of OSL depletion index did show some discrimination between low sensitivity irradiated material and unirradiated samples. Further exploration of this technique would be very useful.

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1. INTRODUCTION

Project A05010 aims to explore means of improving the performance of photostimulated luminescence (PSL) analysis methods for detecting irradiated ingredients in dietary supplements.

UK regulations (HMSO 2000a,b,c, 2001, 2002 a,b) implementing European Directives (EC1999a,b) on food irradiation impose controls on irradiation plant, permitted food treatments, imports of irradiated food and labelling. Food irradiated within the EU must conform to national authorisations, which are mutually recognised within the community, and must be labelled. Irradiated food imported to the EU must have been treated at a recognised facility and must also be labelled. EN standard methods to detect irradiated foods have been developed based on physical, chemical and biological approaches (EN 1996a-d,2000,2001a-d,2002, 2003a,b), some of which are used in market surveys collated annually by the European Commission in keeping with the directives. Reports from the period 2001-2006 (EC 2002,2004, 2006a,b, 2007, 2008) show persistence of undeclared irradiated food, detected using luminescence and other methods. In particular, dietary supplements and their ingredients, first reported by the UK in 2002 (FSA,2002), continue to be detected using luminescence methods despite efforts to remove such irradiated products from the supply chain.

Dietary supplements, or food supplements, and their ingredients represent a diverse product range, incorporating raw or processed plant and animal derived materials, together with anti-caking agents, excipients, encapsulants, and formulations for production of pills, capsules and liquids. Irradiation has the functional ability to control microbial activity while causing minimal damage to pharmacologically active ingredients, many of which are of high value. It can also be used to secure high standards of sterility in inactive phases of pharmaceutical formulations. However, for supplement products regulated under food law, the incorporation of irradiated materials would require extension of the approved product lists for irradiation. In the absence of such approvals, and the inclusion of unambiguous labels, radiation treatment of products or ingredients in this class for sale in the UK remains illegal. Detection methods are in use both by regulatory authorities and by producers and suppliers to reduce the presence of undeclared irradiated produce in the market. Of these the luminescence methods are most widely applied, with initial PSL analysis frequently used to select samples for subsequent TL confirmation.

In the first stage of this project (Sanderson et al 2008) the performance of PSL and TL methods applied to dietary supplement products was reviewed, using data sets from official surveys conducted between 2001 and 2005, and also from the SUERC analytical data base. Some 427 samples from official surveys were examined, where both PSL screening and TL analysis had been applied. Of these calibrated PSL data were available from 280 samples. A further 554 analyses from the SUERC archive were also considered where PSL and TL measurements had been made together. These data were used to examine the incidence of all pairs of possible outcomes for PSL screening and TL analysis. For those samples with calibrated PSL data sample sensitivity was related to the results. Depending on which data set was used, outcomes were identified where PSL screening failed to detect material that subsequently yielded a positive TL result in 5-8% of analyses.. Similarly, in 9-16% of analyses with negative PSL screening, TL analysis subsequently

detected an irradiated component. As expected, the calibrated PSL data confirmed that low sensitivity was associated with many of these instances. For these samples, whose very low mineral contents and correspondingly low PSL sensitivities limit the effectiveness of rapid PSL screening, it is possible that pre-concentration of minerals may improve the performance of PSL. This is investigated further in this part of the project, where simple concentration procedures have been developed and characterised to enhance PSL sensitivity from dietary supplement ingredients.

Other PSL-TL correspondence combinations of interest are that some 4-13% of PSL intermediate screening outcomes were associated with negative TL results. In many of these cases the PSL signal was associated with residual, geologically induced, luminescence, identified by significant TL signals in the high temperature (>300°C) region. A further 2-4% of samples gave positive band PSL results which again were not corroborated by TL analysis. Some of these may arise from PSL carrying components which are water or acid soluble, and therefore not present in normal TL separates. In these cases the PSL outcome may very well be correctly identifying irradiated material which is not readily amenable to analysis by EN1788 TL. However in the case of the geological residuals it would also be beneficial if additional parameters could be identified in PSL analysis to further enhance the discrimination between recent ionising radiation and geologically induced signals. In this study two possibilities have also been examined: the use of depletion rate analysis of the PSL signals, and the effect of varying stimulation wavelength.

This report presents the results of investigations of pre-concentration methods, to improve PSL performance for low sensitivity samples, and an assessment of depletion rate analysis and dual-wavelength PSL stimulation to enhance discrimination between geological and modern signals. Ten dietary supplement herbal ingredients were used for these investigations, retained from FSA Project E01068, and known from that project to exhibit a range of sensitivities. Since many supplements make use of extracts, one of the most common (*Gingko biloba*) was purchased specifically for the current project, together with a common excipient (precipitated silica). These products were prepared in both irradiated and untreated forms. The following sections present work on pre-concentration experiments with these materials, followed by investigations of depletion rates, and finally the potential of multi-wavelength PSL.

2. PRE-CONCENTRATION OF MINERALS

The approach envisaged in the project proposal was to assess the effectiveness of pre-concentration procedures based on the first stages of TL sample preparation. In particular the work-plan intended to examine whether simple settling of dispersed materials in a liquid would provide sufficient mineral concentrations to enhance PSL sensitivity or whether additional steps such as density separation would be needed.

Prior to implementing this plan it was decided to consult with expert PSL users, using the participants list from the recent FSA Proficiency Testing project and other laboratory contacts to assess whether there were other more promising avenues for practical examination. A simple questionnaire was distributed to some 50 laboratories asking whether they had conducted or planned work on pre-concentration to enhance PSL sensitivity, and also enquiring as to the outcomes of work in hand, or opinions as to the most promising approaches. Physical and chemical techniques were suggested to consultees, but they were particularly invited to make their own suggestions. The responses indicated a general interest in this area, but none of the respondents had taken practical steps to enhance the method. While some interest was expressed in chemical digestion, including enzymatic approaches, most of those responding considered that physical methods such as those originally envisaged would be the most worthwhile for initial investigations. A video conference with FSA was also used to explore other potential approaches, and finally the decisions were taken to follow the original workplan and explore liquid settling with and without density separation. Bearing in mind that PSL measurements can be made with wet samples it was felt that both approaches could be conducted efficiently.

In assessing the success of pre-concentration methods to enhance PSL sensitivity it was decided to utilise a concentration factor defined as the relative PSL signal achieved after sample concentration divided by the PSL signal achieved in analysis of untreated material. Since PSL signal levels are highly variable from aliquot to aliquot, due to the varying mineral loads present in the surface layers of samples undergoing screening, and also vary from product to product, it was important to replicate both products and samples per product. After discussion with FSA it was decided to utilise 10 different products, derived from retained materials from the earlier FSA PT study. These were know to have diverse PSL sensitivities, and were available in sufficient bulk to conduct replicated separations. The products available were Siberian ginseng, Alfalfa, Green tea, Saw palmetto, Guarana, Milk thistle, Dandelion, Dong Quai, Echinacea and *Gingko biloba*. A further sample, of *Gingko biloba* extract, was purchased to enable assessment of the behaviour of an ethanolic extract to be included. Sub-samples of all these products, together with some precipitated silica excipient, were irradiated to a dose of 8 kGy, so that both irradiated and untreated samples could be examined. It was decided to develop the concentration procedure using irradiated and unirradiated paprika standards, and then to perform concentration factor measurements from all products in irradiated and unirradiated condition with ten-fold replication.

2.1 General overview of experiments

As described above, a significant proportion of cases in the data set where PSL and TL outcomes differ can be attributed to low sensitivity as indicated by low calibrated PSL measurements. The absence of sample preparation in the EN13751 standard method enables measurements to be made quickly and easily, but also means that a sample petri dish will contain a relatively small number of mineral grains in a much larger quantity of matrix, and that only some of the minerals (those at or near the top surface) will be stimulated and measured. It seems reasonable, therefore, to expect concentration of the mineral load of a sample to enhance the signal observed by PSL, potentially taking the terminal counts over the negative/intermediate threshold.

A series of experiments was therefore designed, based on a decision tree in Appendix C, to investigate whether this is achievable and if so whether it is achievable without compromising the advantages of PSL (speed, ease of sample preparation, easily assimilated techniques).

A series of quick, initial experiments was performed to enable a procedure to be written for multi-sample, multi-aliquots tests using the irradiated paprika standard issued with the PSL instrument. This material was chosen because it is known to have a substantial signal and is available in bulk at SUERC, already characterized.

Following that, an experiment was designed to compare two separation protocols using 10-fold replication with each of the materials retained from Project E01068, in both irradiated and unirradiated form (a total of 400 separations and 800 PSL measurements); blue PSL measurements were also undertaken on the end-products of the more sophisticated separation method, which were also used for depletion rate analysis. Further separations using the density separation method were performed (on duplicate aliquots only) for each product, irradiated and unirradiated, for red/blue PSL measurement on the new portable OSL reader.

Finally, experiments were performed with 2-fold replication on the excipient and extract purchased for this project. For both irradiated and unirradiated samples, red-blue analyses were performed on the unseparated material. Further aliquots of the *Gingko biloba* extract were then separated, half with the established density separation technique used for all products, and half using a modification of the settling method, with ethanol replacing water as the settling (and in this case partial solution) medium.

2.2 Exploratory work on pre-concentration

Using the paprika standard material (SP11627, purchased November 2007, irradiated by Isotron in January 2008 to 8 kGy), comparisons were made between different separation methods. Variables included sample size, whether or not the material was sieved, whether it was treated with ultrasound and if so for how long, volume of water used for settling, and settling time. It was not expected that the optimum method for paprika could necessarily be transferred to other materials, but the experiments were useful for establishing some basic decision-making. A sample flow chart (for experiments using an ultrasonic bath) is shown below in Figure 2.1.

```
                    ┌──────────────┐
                    │  10g paprika │
                    └──────────────┘
                           │
                          PSL1
                           │
                           ▼
                 ┌────────────────────┐
                 │   100ml water in   │
                 │    250ml beaker;   │
                 │    shake and stir  │
                 └────────────────────┘
                           │
                           ▼
                 ┌────────────────────┐
                 │  Settle for 2 mins │──────────▶ Residue to PSL2
                 │      Decant        │
                 └────────────────────┘
                           │
                           ▼
                 ┌────────────────────┐         Sieved fraction
                 │    150µm sieve     │──────────▶ >150µm to PSL3
                 └────────────────────┘
                           │
                        <150µm
                           │
                           ▼
                 ┌────────────────────┐
                 │  l water in 250ml  │──────────▶ Residue to PSL4
                 │ beaker; shake and  │
                 │   settle 2 mins    │
                 └────────────────────┘
                           │
                           ▼
                 ┌────────────────────┐
                 │ Settle for 10 mins │──────────▶ Residue to PSL5
                 │      Decant        │
                 └────────────────────┘
```
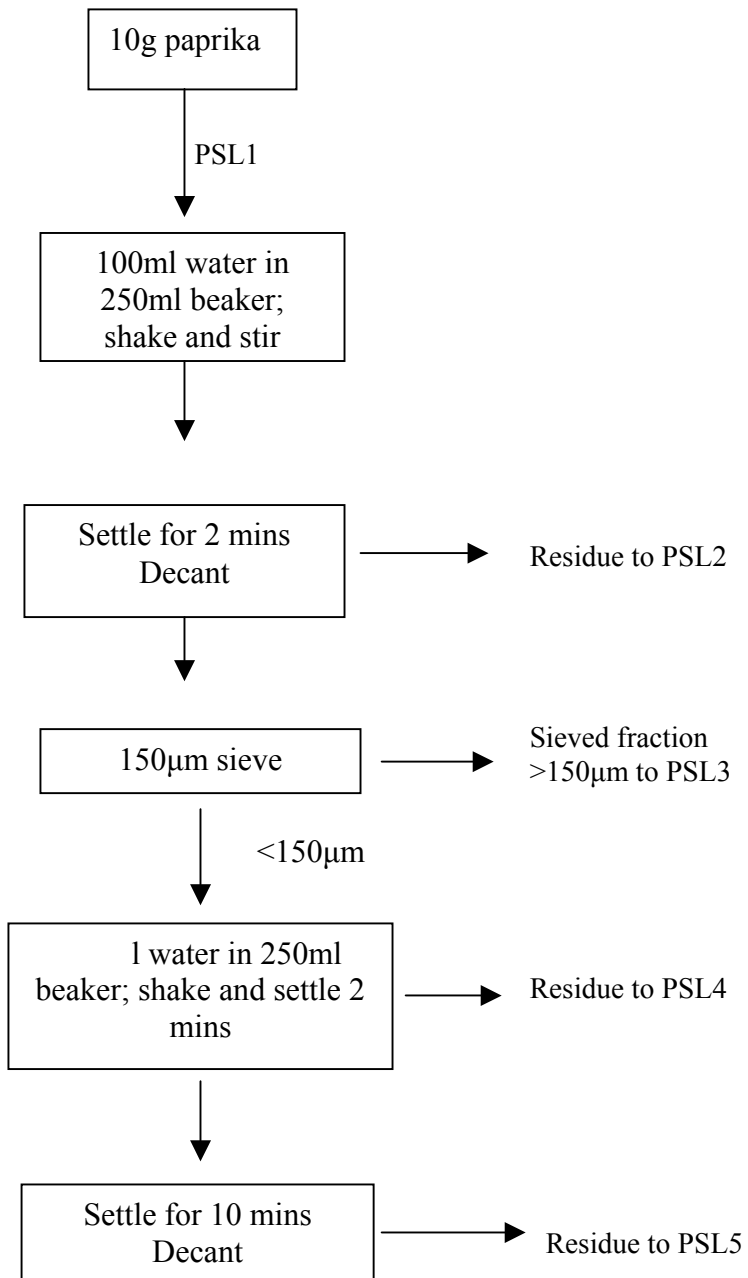
Question : do PSL2, 3, 4 and 5 >> PSL1?

Figure 2.1: Flow chart for signal enhancement experiments

A sequence of PSL measurements (PSL1, PSL2 etc) was made at different stages in the process to assess which variables had the greatest effect.   It was apparent from the amount of signal still obtainable from both size fractions that sieving with a mesh of 150µm does not make a significant difference and this step was not used in subsequent experiments. Settling for periods of 2, 5, 10 and 180 minutes were used on unsieved material; overnight settling was also investigated. Periods of 5, 10 and 30 minutes ultrasound treatment were tried; in the final protocol 5 minutes was chosen. Samples of 2, 5 and 10g were examined; initially a 10g sample was preferred, but due to the density of many of the products used in the main investigation, it was not possible to fit 10g into a petri dish, so the mass was

reduced to 5g. Comparison was also made with a simple density separation (sample mixed with sodium polytungstate – other heavy liquids might be possible – then centrifuged and washed with water) omitting the acid wash and acetone rinse stages of EN1788.

PSL1	Initial reading 10g	119826
	Mixed with 100ml water, settled 2 mins	
PSL2	Residue after liquid decanted	24337
	Decanted liquid sieved 150μm	
PSL3	Residue on mesh	59690
PSL4	Solids settled after 2 mins	16175
PSL5	Solids settled after 10 mins	45206
PSL6	Combined rinsings from all beakers	100521
	Residues given ultrasonic treatment	
PSL7	Settled for 2 mins	114475
PSL8	Settled for 10 mins	258298
PSL9	Settled for a further 10 mins	128109

Table 2.1 Results of experiments with and without sieving and ultrasound, with various settling times, showing that some signal remains in the liquid in all cases.

It was also discovered that the bases of the petri dishes are not all perfectly flat, leading to a migration of mineral grains to the base of the wall, since the sample was wet when dispensed. During the main phase of the investigation aluminium planchets were used inside the petri dishes and provided a level surface for the grains.

Table 2.2 shows the results of a series of PSL measurements taken after ultrasound in 100ml deionised water for 5 minutes; 3 separate samples were made up to 500ml in deionised water and then settled for 2, 10 and 30 minutes. The two longer settling periods produced volumes of residue which would not fit in a single petri dish. The material was therefore split between dishes.

From these two tables it can be seen that initial attempts to enhance the PSL signals by settling minerals in water have not achieved the desired result, although concentration was achieved when final washing was conducted carefully. It is assumed that even with a material known to be irradiated and highly sensitive, not all the signal produced will reach the photo-multiplier tube, if there is a significant overburden of organic material. Based on these initial experiments there should be scope for further enhancement.

		Sample		
		A 2 mins settle	B 10 mins settle	C 30 mins settle
PSL1	Initial reading	107058	89863	105705
PSL2	Readings from residue after 5mins ultasound then settling	41610	37156	19654
	Excess residue divided between 2 (B) or 3 (C) dishes		42307	34799
				44097
	Petri dishes left to settle 1 hour			
PSL3	Readings from residue after settling with water pipetted off	37135	24703	22960
			35422	23982
				185202
PSL4	Readings from solids settled from pipetted water	35971	17952	22968
	All residues for each sample recombined, settled 2mins, decanted, residue washed and decanted			
PSL5	Recombine, settle and wash cycle	366303	675390	864200
PSL6	Residue from last washing from PSL5	420686		
PSL7	Residue from 180mins settling, residue washed and decanted	323599	1104126	325948
PSL8	Final settling from liquid decanted from PSL7	36137	84916	510397

Table 2.2 Results of variable settling times with ultrasound

The next experiment conducted tested 3 different periods of ultrasound agitation (5, 10 and 30 minutes) in 500ml deionised water and a 5 minute agitation in 100ml deionised water followed by the addition of more deionised water up to 500ml, 2 minutes settling and then rinsing. During the rinsing process, the beaker was swirled to create a vortex and then the liquid was poured off. Results from this experiment are presented in Table 2.3, from which it appears that there is no advantage to be gained, and possibly even a disadvantage, with longer agitation times. Subsequent experiments therefore used 5 minutes agitation only.

Table 2.4 shows the results of introducing a density separation using sodium polytungstate at a density of 2.0 as suggested by EN1788. It can be seen that this step does result in a concentration factor of up to 10, except after overnight settling, which suggests that some of the organics fall through the column of water given sufficient time.

		Sample			
		A 5mins u/s	B 10mins u/s	C 30mins u/s	D 5mins u/s; 30mins settling
PSL1	Initial reading	95046	110253	93164	223409
PSL2	After ultrasound	190575	104559	70948	110123
	After settling cycle		74210	332723	77629
	Repeat settling		107233		

Table 2.3 Effect of variable periods of ultrasonic agitation (u/s)

		Sample		
		A	B	C
PSL1	Initial reading (2g samples)	83168	84639	63013
PSL2	30 mins settling	76483		
	Density separation after 30 mins settling		518250	
	Density separation, no settling			625075
PSL3	Residue after overnight standing	23306		
	Plus density separation		48980	

Table 2.4 Use of density separation with and without settling

From these initial experiments it can be seen that introducing steps from the TL mineral separation procedure is probably the most effective way of enhancing a PSL signal. These experiments were however performed on a high sensitivity product, known to have been irradiated. Further experiments are required, with a range of products, before firm conclusions can be drawn. It was not practical within this project to examine all the products and product types covered by the surveys reviewed at the start of the project. There was, however, no clear correlation between product form (eg powders, capsules, tablets), number of ingredients or nature of the herbal precursor (roots, leaves, flowers, for instance) within the data set examined.

Paired protocols were devised for use with the samples available from Project E01068, to compare a settling regime with a density separation; this is described below.

2.3 Measurement of Concentration factors for 10 dietary supplement ingredients

2.3.1 Sample details

As noted above the ten products available in bulk (5kg purchased in March 2007) for this part of the project were:

SP10950	Siberian ginseng
SP10951	Alfalfa
SP10952	Green tea
SP10953	Saw palmetto
SP10954	Guarana
SP12334	Milk thistle
SP12335	Dandelion
SP12336	Dong quai
SP12337	Echinacea
SP12338	*Gingko biloba*

All these were purchased from Cambridge Commodities Limited, and the first 5 were used in Project E01068 to create blends. The remaining products were not used at that time, and were only allocated SUERC sample numbers for the current project.

A further sample, SP12339 *Gingko biloba* extract, was purchased in December 2008 from Gee Lawson to enable assessment of the behaviour of an extract as opposed to herbal powders which are equivalent to herbs and spices.

Sub-samples of all these products, together with some precipitated silica excipient purchased from Fischer, were irradiated at Isotron Limited in December 2008; they received a dose of 8 kGy.

It had been observed during Project E01068 that the bulk sample of Siberian ginseng did not appear to be the same product as the portion purchased at the same time dispensed into plastic tubs. The bulk material displayed exceptionally low luminescence sensitivity and was believed to be an extract, mistakenly supplied in place of a herbal powder. The material was nevertheless used for the current project, and provides results with 10-fold replication for one extract; the declared extract SP122339 was only tested in duplicate.

Working through the two protocols in parallel (a total of 20 aliquots per sample), each product was examined on a separate day. All the irradiated materials were tested, then all the unirradiated materials. This aimed to minimize the risk of cross-contamination. All preparation was performed in a laminar flow cabinet.

2.3.2 Measurement Protocol

The protocol for the settling method was as follows:

1. Dispense and weigh 10 portions of the material into petri dishes (5 or 10g approximately, depending on the density of the product).
2. Perform PSL measurements of these samples (60 seconds) – record results as PSL1A

3. Decant the powder from each petri dish into a separate beaker and make up to 500ml with deionised water
4. Treat with ultrasound for 5 minutes
5. Allow to settle in the beaker for 30 minutes
6. Decant the standing liquid briskly and discard
7. Make the residues up to 100ml with deionised water
8. Allow to settle for 2 minutes
9. Decant the liquid again
10. Rinse the residues, which should consist of minerals with only a small amount of organic matter still present
11. Using the vortex swirling technique described above, pour the minerals, with as little water as possible into a planchet inside the petri dish
12. Repeat the PSL measurement recording the results as PSL2A

For the density separation, the protocol was as follows:

1. Dispense and weigh 10 portions of the material into petri dishes (5 or 10g approximately, depending on the density of the product).
2. Perform PSL measurements of these samples (60 seconds) – record results as PSL1B
3. Decant the powder from each petri dish into a separate beaker and make up to 100ml with deionised water
4. Treat with ultrasound for 5 minutes
5. Decant the contents of each beaker into 4 centrifuge tubes
6. Centrifuge to separate the solids from the water
7. Decant the liquid and discard
8. Add approximately 30ml sodium polytungstate at a density of 2.0
9. Treat with ultrasound for 5 minutes
10. Centrifuge to separate material which floats from material which sinks
11. Decant and recycle the tungstate
12. Rinse the minerals remaining in the centrifuge tubes following steps 8-11 of the settling protocol, combining the contents of the 4 tubes into a single portion for dispensing into the planchet
13. Repeat the PSL measurement but extend the measurement for 300s recording the results as PSL2B

2.3.3 Results from 10 herbal supplement products

For each product, a number of statistics were derived from the data. Individual PSL files from the 300 second measurements were corrected where applicable for counter overflow, and the 60-second measurements recorded. It was then possible to calculate a Concentration Factor (CF) for each product by dividing the PSL2 60 second measurement by the PSL1 terminal count, recorded after 60 seconds. The reason for prolonging the final PSL measurement following density separation for 300s was to generate data from these extracts which could be used for depletion-rate analysis without the need to conduct further separations. This is discussed further in section 3.

For each product, means and standard deviations were calculated for the raw data, the $\log_{10}$ of the raw data and the ratios described above. (The $\log_{10}$ values for the ratios are

presented as the logarithms of the quotients, not the quotients of the logarithms.) These results are tabulated in Appendix A together with data from each sample of each product. Tables 2.5 and 2.6 below show the mean counting data and standard deviations for each product in irradiated and unirradiated form at both stages of separation. These are also shown in figures 2.2 and 2.3.

	1 stage settling		2 stage settling + density separation	
	Initial PSL	PSL after settling	Initial PSL	PSL after density separation
Siberian ginseng	488 ± 136	1038 ± 461	506 ± 144	4580.2 ± 3013
Alfalfa	2160861 ± 111406	6386830 ± 2637506	2073918 ± 198107	17512788 ± 5155609
Green tea	43930 ± 12002	230460 ± 146089	40690 ± 8220	511893 ± 224157
Saw palmetto	1650 ± 467	2849 ± 3751	1980 ± 723	14315 ± 6836
Guarana	19035 ± 9570	20391 ± 17773	13035 ± 3524	53522 ± 37259
Milk thistle	127298 ± 18614	42650 ± 20123	129034 ± 19469	190655 ± 64103
Dandelion	2265364 ± 120154	8659487 ± 2665796	2184000 ± 163892	23113485 ± 3759105
Dong quai	3071532 ± 160096	4325139 ± 1430796	3118568 ± 251468	8960559 ± 2284501
Echinacea	31582 ± 8437	198682 ± 86702	34311 ± 6109	818113 ± 276125
Gingko biloba	720830 ± 46984	2327672 ± 1276712	799650 ± 52483	6259060 ± 1423245
Global	844257 ± 1132473	2219520 ± 3283384	839569 ± 1124840	5743897 ± 8255544

Table 2.5 Mean terminal counts and standard deviations for irradiated products before and after pre-concentration

	1 stage settling		2 stage settling + density separation	
	Initial PSL	PSL after settling	Initial PSL	PSL after density separation
Siberian ginseng	280 ± 36	288 ± 40	315 ± 67	286 ± 61
Alfalfa	1964 ± 296	3906 ± 1489	1730 ± 146	14668 ± 2946
Green tea	501 ± 68	341 ± 38	464 ± 49	593 ± 294
Saw palmetto	326 ± 82	317 ± 82	271 ± 35	341 ± 68
Guarana	492 ± 112	431 ± 227	513 ± 148	2555 ± 1130
Milk thistle	3120 ± 874	636 ± 356	4031 ± 2642	5620 ± 3252
Dandelion	4528 ± 3592	10474 ± 5830	3264 ± 413	4717 ± 2631
Dong quai	2717 ± 1300	4669 ± 2117	2956 ± 2050	3055 ± 2762
Echinacea	322 ± 46	349 ± 70	328 ± 36	397 ± 114
Gingko biloba	811 ± 623	1132 ± 1006	621 ± 198	2603 ± 1803
Global	1506 ± 1867	2254 ± 3706	1449 ± 1714	3483 ± 4557

Table 2.6 Mean terminal counts and standard deviations for unirradiated products before and after pre-concentration

Irradiated samples
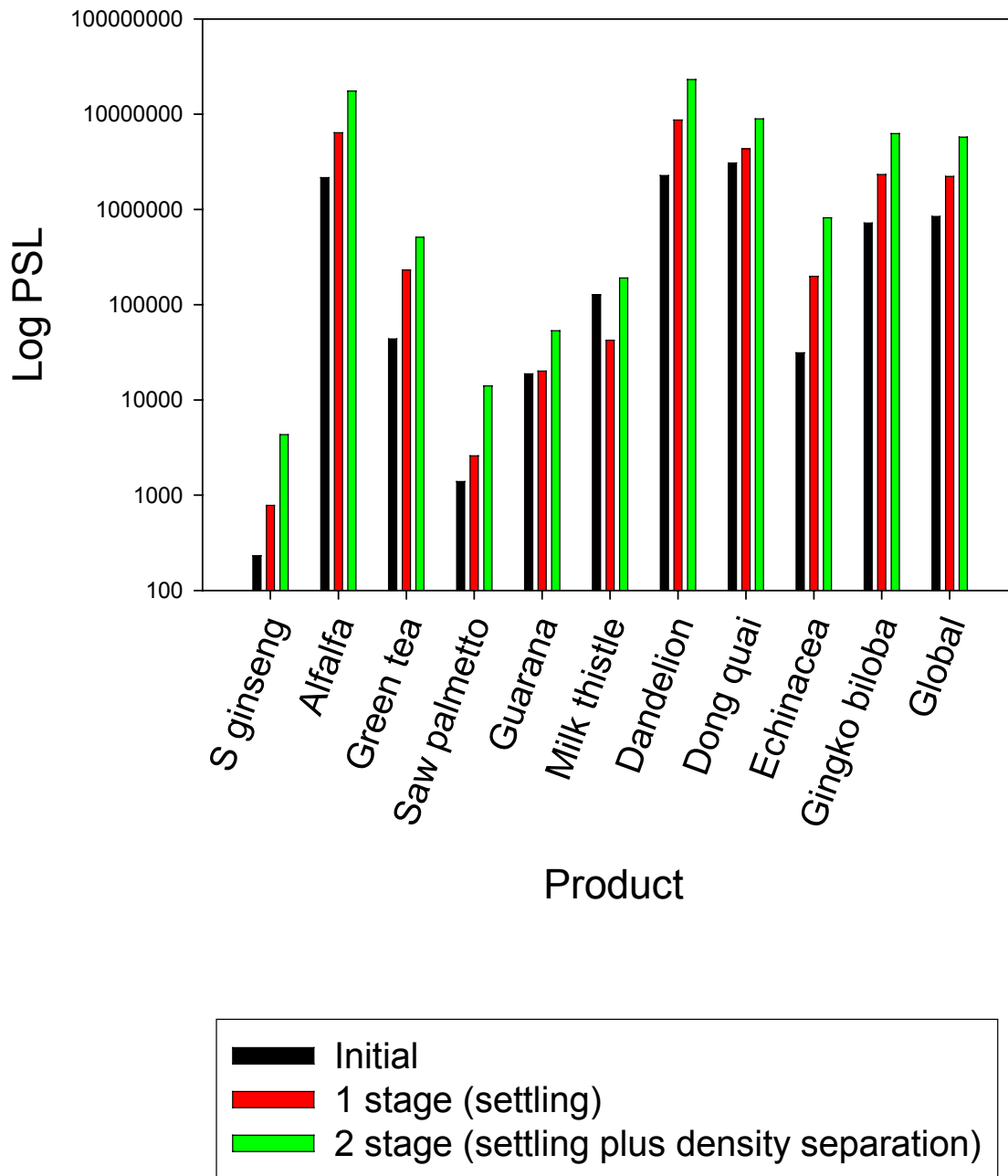
Figure 2.2 PSL screening data from irradiated samples before and after single stage or two stage settling

Unirradiated samples
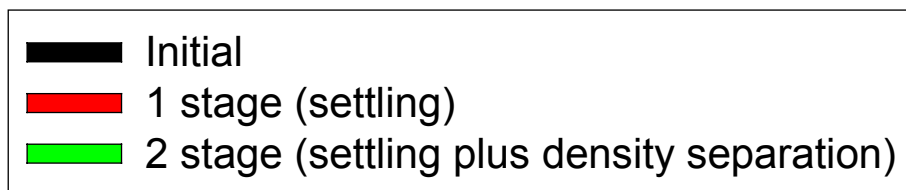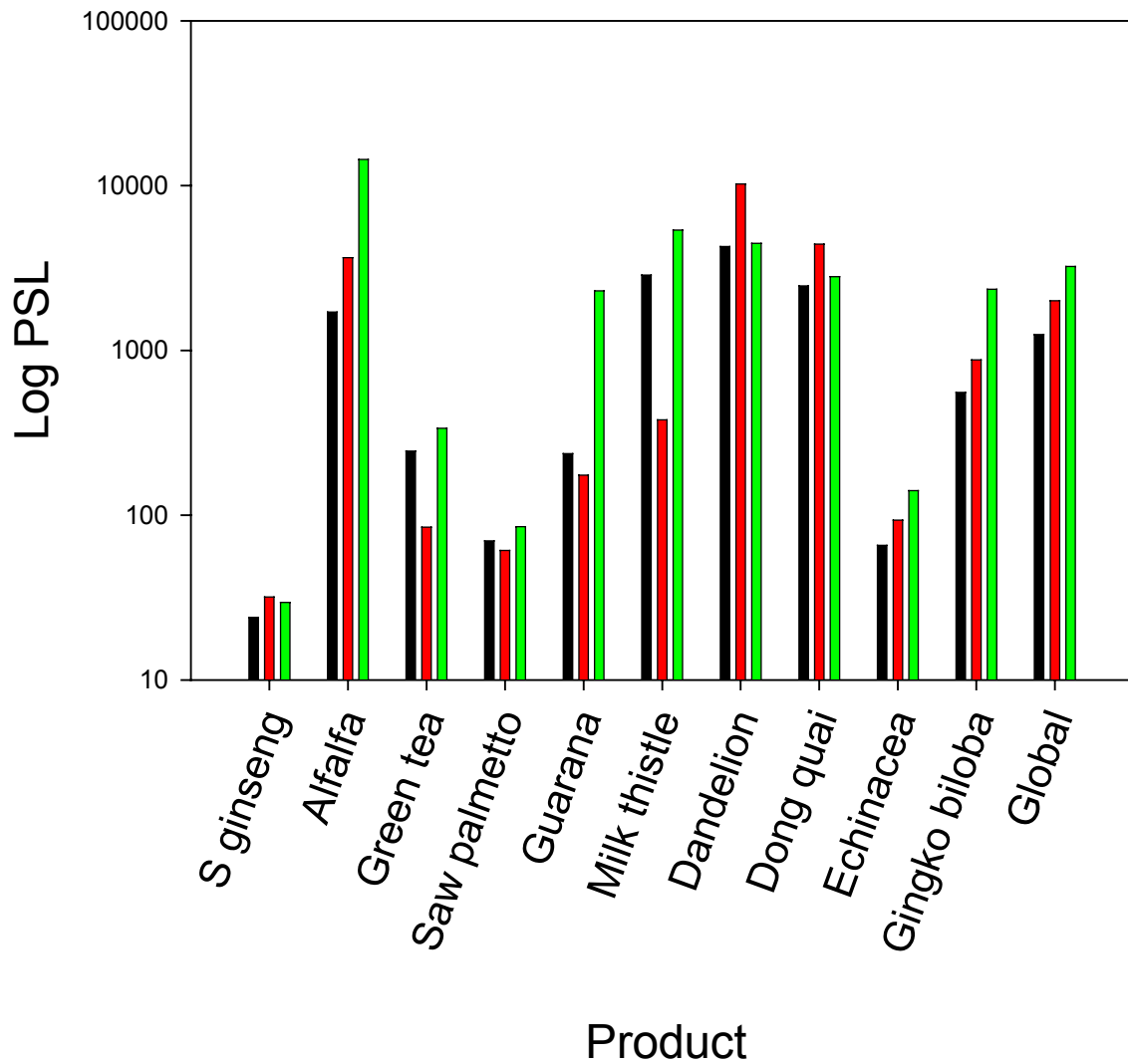
Figure 2.3 PSL screening data from unirradiated samples before and after single stage or two stage settling

Table 2.7 shows the mean concentration factors and standard errors obtained from the experimental results in both one-stage and two-stage separation methods. Bearing in mind that each of these mean factors has been derived as the mean of 10 pairs of sample analyses, each of which exhibits considerable natural variation, it is unsurprising to find significant variations in the concentration factors achieved. However several observations can be made despite this, which suggest both process and sample specific differences. Firstly it is evident that the 2 stage process achieves higher concentration factors under the experimental conditions used than simple water separation. For irradiated samples the mean factor is over 10 compared with 3-fold mean concentration for the single stage process. This is consistent with the findings of the exploratory work with paprika, and is believed to reflect the overlapping settling times of larger size organic materials and the finer mineral debris, which limits the effectiveness of settling alone in achieving a high

Irradiated samples	1 stage settling Concentration Factor (± SE)	2 stage settling + density separation Concentration Factor (± SE)
Siberian ginseng	3.86 ± 0.75	22.67 ± 6.62
Alfalfa	2.92 ± 0.35	8.56 ± 0.87
Green tea	5.82 ± 1.45	13.43 ± 2.38
Saw palmetto	1.57 ± 0.54	10.07 ± 2.52
Guarana	1.10 ± 0.21	4.35 ± 0.99
Milk thistle	0.33 ± 0.04	1.46 ± 0.12
Dandelion	3.83 ± 0.38	10.61 ± 0.57
Dong quai	1.41 ± 0.15	2.87 ± 0.21
Echinacea	6.58 ± 0.95	24.33 ± 2.64
Gingko biloba	3.24 ± 0.56	7.87 ± 0.62
Global	3.07 ± 0.28	10.62 ± 1.07

Unirradiated samples	1 stage settling Concentration Factor (± SE)	2 stage settling + density separation Concentration Factor (± SE)
Siberian ginseng	0.62 ± 0.60	1.81 ± 4.86
Alfalfa	2.14 ± 0.25	9.76 ± 0.52
Green tea	0.36 ± 0.05	1.74 ± 0.53
Saw palmetto	3.68 ± 4.23	1.16 ± 4.47
Guarana	0.96 ± 0.44	10.97 ± 2.11
Milk thistle	0.15 ± 0.05	1.63 ± 0.31
Dandelion	3.04 ± 0.55	1.51 ± 0.27
Dong quai	1.92 ± 0.27	1.18 ± 0.42
Echinacea	1.99 ± 0.87	2.92 ± 0.98
Gingko biloba	2.65 ± 1.16	8.33 ± 2.74
Global	1.75 ± 0.45	4.09 ± 0.81

Table 2.7 Concentration Factors for each product and both methods

concentration factor. For unirradiated samples there is also a higher concentration factor for the 2 stage process than simple settling based separation, but interestingly the concentration factors achieved are somewhat lower than those obtained from irradiated samples. It can also be seen that concentration factors vary from product to product within each group. Figure 2.4 illustrates the concentration factor data in graphical from which most of these trends can be clearly seen.

	Concentration factor ratios			
	Irradiated/Unirradiated		2 stage/1 stage separation	
	1stage	2stage	irradiated	unirradiated
Siberian ginseng	6.25	12.50	5.87	2.93
Alfalfa	1.37	0.88	2.93	4.57
Green tea	16.14	7.70	2.31	4.84
Saw palmetto	0.43	8.66	6.41	0.32
Guarana	1.15	0.40	3.94	11.42
Milk thistle	2.13	0.89	4.43	10.60
Dandelion	1.26	7.05	2.77	0.50
Dong quai	0.73	2.44	2.03	0.61
Echinacea	3.30	8.32	3.70	1.47
Gingko biloba	1.22	0.94	2.43	3.14
Mean	3.40	4.98	3.68	4.04
Std err	1.44	1.31	0.45	1.21

Table 2.8 Comparison of the Concentration Factor ratios for Irradiated and Unirradiated samples, and for 2 stage and 1 stage separations

Table 2.8 draws the two main features out further by presenting the concentration factor ratios between 1 stage and two stage separations, and between irradiated and unirradiated samples, for each product and for the mean. From this it can be seen that, regardless of separation method, irradiated samples appear to respond to concentration some 3-5 times more readily than untreated materials. Also the 2 stage process is some 3-4 times more effective than the single stage process regardless of whether the sample had been irradiated. In respect of the observation that irradiated samples produced higher concentration factors than unirradiated samples it appears to be easier to enhance an already substantial signal. It may be the case that the irradiation process has a physical effect on the organic phases of the product which makes it easier to separate from the inorganic silicates. Certainly it is sometimes possible to visually distinguish two portions of the same product, one of which has been irradiated; the irradiated portion tends to be darker. Viscosity is also affected. Alternatively, since the number of "extra" minerals produced by the separation processes should not significantly differ between irradiated and unirradiated samples of the same product, perhaps the effect seen is merely a consequence of the fact that, in the irradiated portions, all these "extra" minerals have certainly been exposed to ionizing radiation and are thus potential signal producers, whereas in the unirradiated portion the irradiation history is unknown for all the minerals.
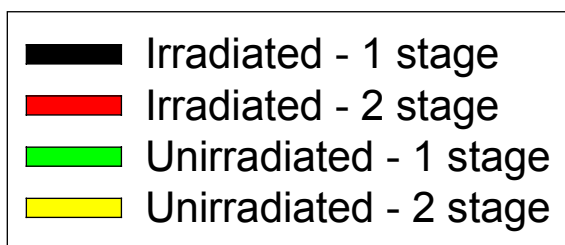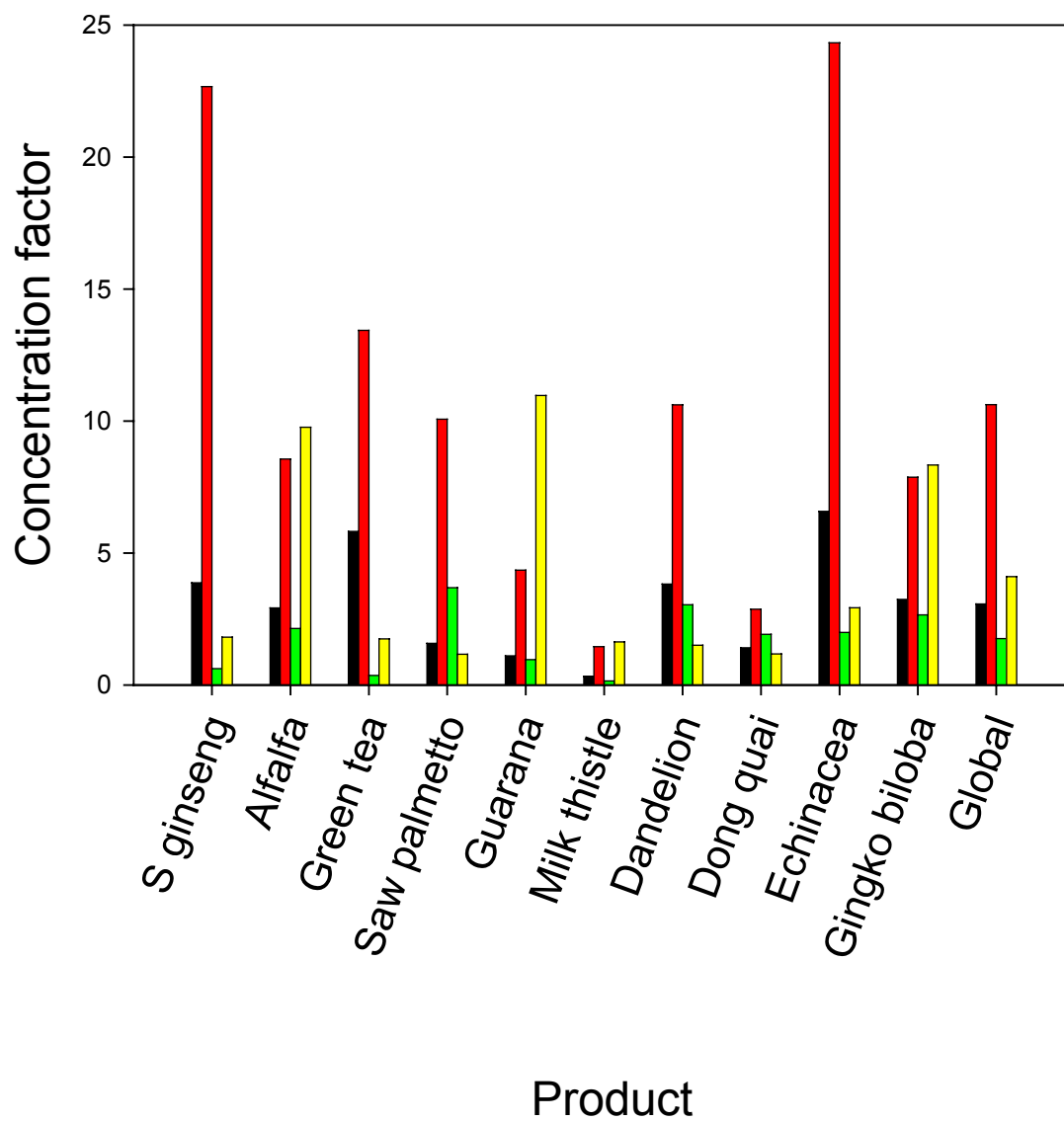
Figure 2.4 Concentration factors achieved after single stage or two stage separations

It can be expected that they will have been exposed to natural radiation, but the extent of this and its homogeneity are not quantified.

One of the products where density separation does not lead to a higher concentration than settling, Siberian ginseng, differs in physical form from the other product used and produced a white precipitate (presumably an excipient) during separation in both methods which was difficult to separate from the desired silicate fractions, potentially affecting the PSL measurement. There is no obvious reason why the other two products, dandelion and dong quai, also go against the trend. Figure 2.4 plots mean initial PSL terminal counts for each product against the Concentration Factor for each method and for irradiated and unirradiated materials; there is no clear relationship between the variables. For unirradiated samples, the initial PSL does not vary greatly, but the concentration factors are spread over an order of magnitude. For irradiated samples, in contrast, concentration factors after settling vary less than those after density separation, and there is a spread of initial counts over 6 orders of magnitude as is to be expected from materials of varying sensitivity. The product with a mean concentration factor of 24 is an outlier; without this datum the spread of CFs for irradiated sample is not significantly different for the two methods. It may be, however, that this maximum CF is achievable for more samples if the methods are adapted. This requires further investigation.

For the two methods tested on these products, the Concentration Factors are generally lower than was hoped, being at most one order of magnitude when two might have been expected, given the probable distribution of mineral load in a full petri dish. The increased distance between the measurement surface and the PMT is not likely to be a significant factor, and applies evenly to all samples measured here.

Tables 2.5 and 2.6 confirm that, for some samples, concentration has transformed a negative classification into an intermediate one or an intermediate to a positive outcome. For the irradiated samples in Table 2.5, this only occurs where initial sensitivity is low; those samples which are already positive clearly cannot be promoted. For unirradiated samples, some show an initial signal which has been shifted into another classification band by concentration; with more instances following density separation. No instances were observed of a negative to positive shift.
During the examination of existing data sets in the first part of this project, it was found useful to plot initial vs calibrated PSL terminal counts colour-coded according to combined PSL/TL outcome. This plot is reproduced below as Figure 2.5.

17

PSL/calPSL plot by category
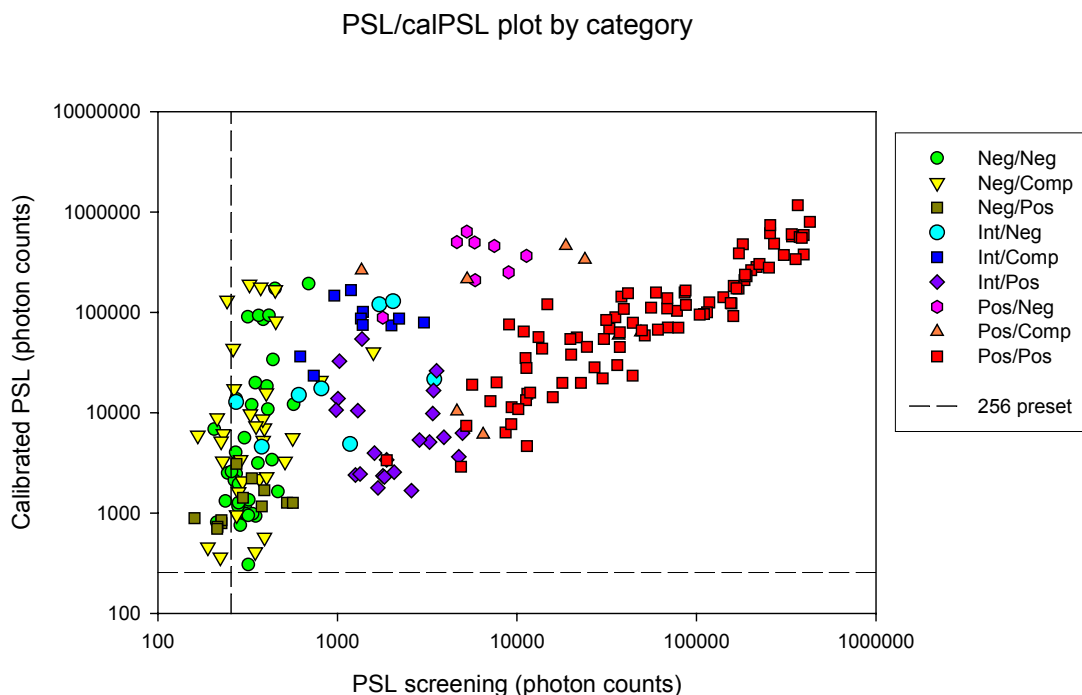
Figure 2.5 Calibrated plot for samples from the existing data sets

Analogously, the data from the settling and density separation experiments can be plotted, using the irradiated aliquots as proxies for calibration of the unirradiated aliquots. Three sets of data points, initial, after settling and after density separation, can be plotted in this way, for all samples (Figure 2.6). Plots for each product separately are in Appendix D (Figures D1-5). As a proxy for calibrated of the unirradiated samples, aliquot 1 unirradiated was paired with aliquot 1 irradiated, 2 with 2 and so on. For the irradiated samples, aliquot 1 plots against aliquot 2, 2 against 3, and so on. Since the aliquots are random sub-samples of the whole and the minerals in the "calibrated" portions differ from those in the "screening" portions, a greater scatter is to be expected than in the genuine calibration plot. This is indeed the case.

Figure 2.6 shows that all the samples plot with a distribution similar to the survey samples, both initially and after treatment. The area of plot 2.5 occupied by positive samples with non-negative TL is more sparsely populated in figure 2.6, as is to be expected from samples which did not include blends. Those with high initial unirradiated counts do tend to also have high irradiated counts, indicating that higher sensitivity products are more likely to display signals in the unirradiated portions. This supports the earlier conclusions about the effect of low sensitivity. It is certainly not the case that all attempts at enhancement have succeeded (particularly not if success is defined in terms of moving a sample into a different PSL classification), or that one method is strikingly better than the other.

All products - initial PSL
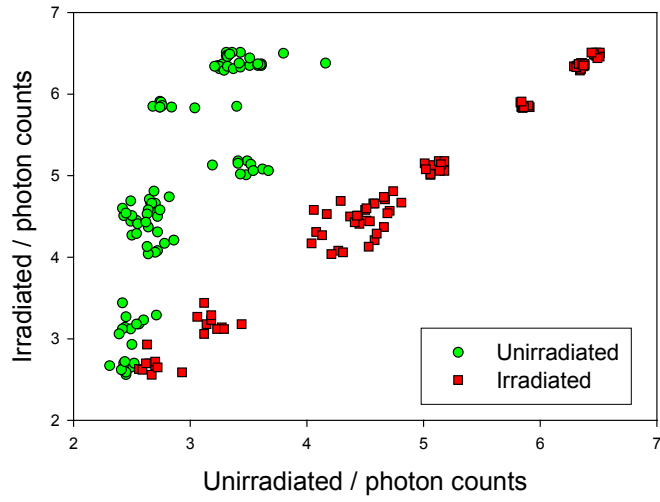
All products - PSL after settling
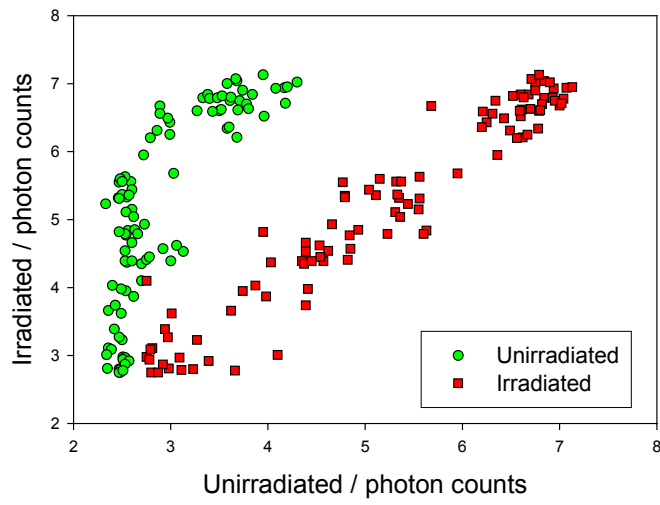
All products - PSL after density separation
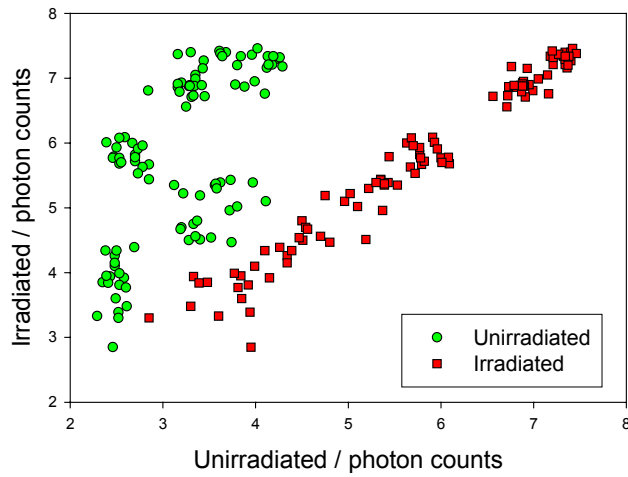
Figure 2.6"Calibrated" plot for all samples initially, after settling and after density separation

Individual plots (Figures D.1-5) for each product show how much product to product variation there is (with implications for a single recommended enhancement method). Alfalfa, milk thistle and echinacea show the clusters according to method that could lead to a recommended procedure; guarana distinguishes the density separation, and all the rest except Siberian ginseng and saw palmetto show some degree of clustering. The Siberian ginseng is in any case different, since it may be an extract with more than one ingredient. In some cases (e.g. green tea) settling has led to a CF of less than one. This suggests that signal-bearing minerals have been discarded in the water (possibly implying that fine particles are responsible for a significant part of the signal). The samples were measured with some water remaining in the petri dishes, and it may be significant that some of the green tea samples concentrated by settling subsequently developed moulds, indicative of the continued presence of an organic fraction.

The interim conclusion is, therefore, that while the introduction of a density separation step into the PSL method might enhance the signal it does not do so routinely with the low sensitivity samples which are perceived to be problematic for this to be a working solution. Further investigation of more complex methods, possibly dependent on the product type, is still required. A step has been taken towards this with the work described below using *Gingko biloba* extract.

2.3.4 PSL signal enhancement of *Gingko biloba* extract

Many dietary supplements contain extracts from plant products, usually in order to concentrate their active ingredients. These extracts are frequently very clean and can be difficult to separate minerals from even with the full EN1788 procedure. Such materials are likely to form a significant percentage of the low sensitivity samples which may give rise to mis-matched PSL/TL outcomes and which may benefit from signal enhancement.

As mentioned above, one of the 10 products (SP10950 Siberian ginseng) used for the settling versus density separation comparisons was an extract, with exceptionally low sensitivity and distinctive behaviour during separation which made it more difficult to apply the methods. Despite this, density separation of the irradiated portion did achieve a mean CF of 9, but with a large standard deviation.

It was initially intended that one or more mixtures would be made, using the *Gingko biloba* extract and a commonly used excipient, precipitated silica. Portions of both these materials were accordingly irradiated at the same time as the remaining products. PSL analysis was performed on two aliquots of each of the proposed components for the mixtures for both irradiated and unirradiated material. Blue measurements were also made. It was then decided that it would be sufficient for the present study to confine further experiments to the extract only, though for future work blends of different proportions could be examined in more detail.

For this part of the project, the same density separation protocol was followed for 2 aliquots of irradiated extract and 2 unirradiated. For comparison, 2 aliquots of each were also treated with absolute alcohol to establish whether dissolution of the vegetable extract might leave behind sufficient mineral grains to make this a worthwhile enhancement method.

All the aliquots used in this part of the project were of approximately 10g mass. Those treated with alcohol were placed in 500ml beakers with 200ml solvent, stirred to dissolve as much as possible, then allowed to settle for 10 minutes. After decanting of the supernatant solution, the solid residue was washed with deionised water as before. It was observed that there was some further dissolution. PSL measurements were made in the same manner as previously.

Irradiated

	Ethanol		Density separation	
Aliquot	1	2	3	4
PSL1	2362	2705	6472	2581
PSL2	32470	95112	44316	66418
CF	13.75	35.16	6.85	25.73

Unirradiated

	Ethanol		Density separation	
Aliquot	1	2	3	4
PSL1	482	395	306	398
PSL2	1545	348	804	997
CF	3.21	0.88	2.63	2.51

Table 2.9 Effect of ethanol solution and density separation on *Gingko biloba* extract. PSL1 is the initial reading, PSL2 the reading after concentration. Highlights indicate promotion from negative to intermediate (yellow) and intermediate to positive (green) as a result of concentration.

From Table 2.9 it can be seen that both methods significantly enhance the signal when the extract has been irradiated, and also that where the initial readings were intermediate, the intermediate/positive threshold has been crossed. This is of limited value, however, since further analysis is recommended for intermediate PSL outcomes as well as positive. For the unirradiated material there is also an increase in 3 out of 4 examples, taking the classification into the intermediate band and thus indicating the need for further investigation. There is no significant difference between the 2 methods, so the simpler and cheaper ethanol dissolution can be considered preferable. The use of ethanol in large quantities is not risk free, however, so it would be useful to continue investigate other solvents and perhaps also other heavy liquids.

2.4 Summary

The aim was to assess the effectiveness of pre-concentration procedures based on the first stages of TL sample preparation. PSL signal levels are highly variable from aliquot to aliquot, due to the varying mineral loads present in the surface layers of samples undergoing screening, and also vary from product to product, it was important to replicate both products and samples per product. 10 different products, derived from retained materials from the earlier FSA PT study were used. These were know to have diverse PSL

sensitivities, and were available in sufficient bulk to conduct replicated separations. The products available were Siberian ginseng, Alfalfa, Green tea, Saw palmetto, Guarana, Milk thistle, Dandelion, Dong Quai, Echinacea and *Gingko biloba*. Work started on irradiated and unirradiated paprika standards, to develop the concentration procedure, and then to perform concentration factor measurements from all 10 products in irradiated and unirradiated condition with ten-fold replication. A series of experiments was performed, to enable a procedure to be written for multi-sample, multi-aliquots tests using the irradiated paprika standard issued with the PSL instrument.

Initial attempts to enhance the PSL signals by settling minerals in water did not achieved the desired result, even with a material known to be irradiated and highly sensitive, not all the signal produced will reach the photo-multiplier tube, if there is a significant overburden of organic material. Results from further experiments using ultrasonic agitation for various times showed no advantage, however the use of a density separation was a more effective way of enhancing the PSL signal.

Two protocols were devised for use with the 10 samples, to compare a one stage settling regime with a two stage settling and density separation. The results show that the 2 stage process achieves higher concentration factors than simple water separation. For the irradiated samples the mean factor is over 10 compared to 3 fold mean factor for the single stage process. For the unirradiated samples there is also a higher concentration factor for the 2 stage process but interestingly the concentration factor is slightly lower than than those obtained for the irradiated products. The results have shown that regardless of separation method, irradiated samples appear to respond to concentration 3-5 times more readily than unirradiated samples. The 2 stage process is some 3-4 times more effective than the single stage process irrespective of the sample status. The introduction of the density separation step into the PSL method may enhance the signals for many products, but it does no do so routinely with low sensitivity samples which are problematic anyway. Further investigation of other methods is required, especially specific to low sensitivity product types.

Extracts from plant products are frequently very clean and can be difficult to separate minerals from even using full EN1788 procedure and may benefit from PSL signal enhancement. Using the *Gingko biloba* extract, the same density separation protocol was followed for 2 aliquots of each status and further 2 aliquots of each were also treated with absolute alcohol and PSL measurements under the same conditions were made. The results show that both methods significantly enhance the signal when the extract has been irradiated and for the unirradiated material there is also an increase in 3 out of 4 examples. No significant difference between these 2 methods was observed.

Overall we are able to enhance the PSL signal from these 10 retained materials from the earlier FSA PT study, using the 2 stage process. We have shown that although some extracts still prove to be problematic, ethanol dissolution can be used to aid the signal. Further investigation using other solvents and also other heavy liquids would be beneficial.

3.DEPLETION RATE ANALYSIS

During the measurement of photostimulated luminescence, the frequency with which photon counts are recorded, and the total number of cycles, can be defined by the user. In standard EN13751 screening measurements, 60 cycles of 1 second duration are normally recorded, with the summary file containing the cumulative count at the end of 60 seconds for each sample and separate data files containing all 60 individual measurements together with errors and the count rate for each second of the measurement. From these data files, therefore, it is possible to extract the cumulative count after any given number of measurements and also to examine the change in the count rate with time. Count rate declines with time. The rate at which this occurs is expected to vary depending on the source of the measured signal, potentially enabling a distinction to be made between materials which have recently been exposed to ionising radiation and those which have only been exposed to natural radiation over far longer periods but at a lower dose rate. Such a distinction might help to reduce the incidence of samples with non-negative PSL classifications being carried forward to expensive TL analysis only to reveal exclusively high temperature signals.

For the present project, measurements of the samples which had undergone density separation were extended to 300 seconds. These samples were chosen since it was expected that in general a density separation would lead to a higher terminal count and therefore also higher counts after any given period, leading to a larger amount of additional information with a longer measurement period.

Counts after 60 seconds were extracted from the data files for use in the statistics described above and also for calculating the 300/60 second ratio for each sample. Examination of the data files also revealed the need for correction of counter overflow for some of the irradiated samples (2^{24} is the maximum which can be registered by the counter before it resets and the counts accumulate again; in some cases 3 or 4 such overflows were observed during 300 seconds).

From these corrected data, it was possible to plot count rate against time. It was decided to present mean depletion rates for each product in its two forms to simplify the graphical image. A global depletion rate for each irradiation category was also plotted, as were means for each products and a global mean, all normalised to the initial reading. This was done because of the very large difference in the magnitude of the initial count between irradiated and unirradiated samples, leading to problems with scaling the graphical representations. It was hoped that these normalised plots might lead to the definition of a parameter which could be used to distinguish irradiated samples from those with signals of purely geological origin.

In the course of plotting these data it was seen that in some cases spikes were present, due either to noisy signals or counter effects. Smoothing by averaging the data either side of each spike was used to eliminate this and make the plots easier to interpret.

Figure 3.1 shows depletion rate and normalised depletion rate for Dong quai; similar plots for all products and a global plot can be found in Appendix D.
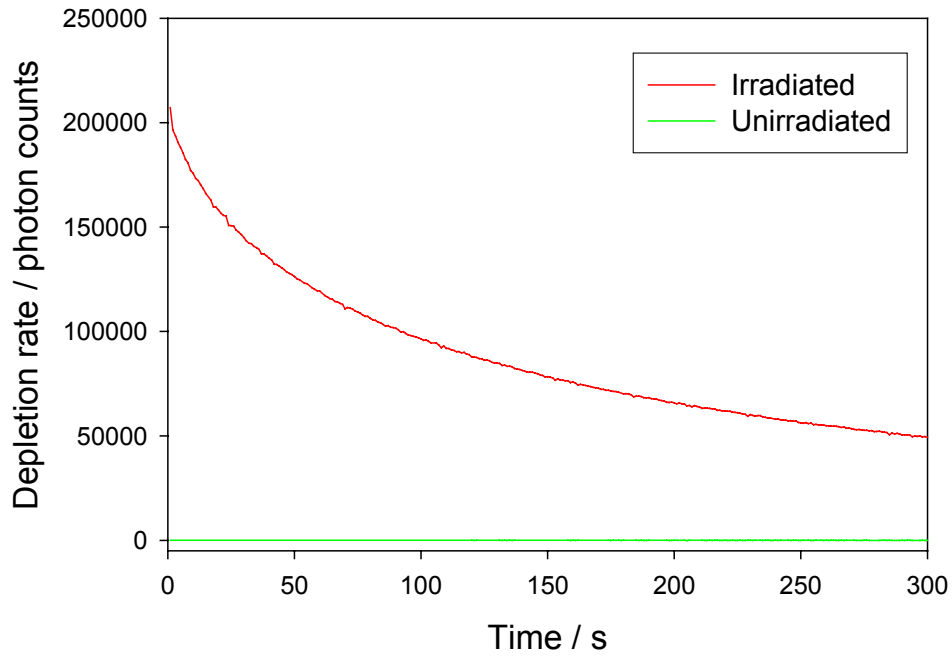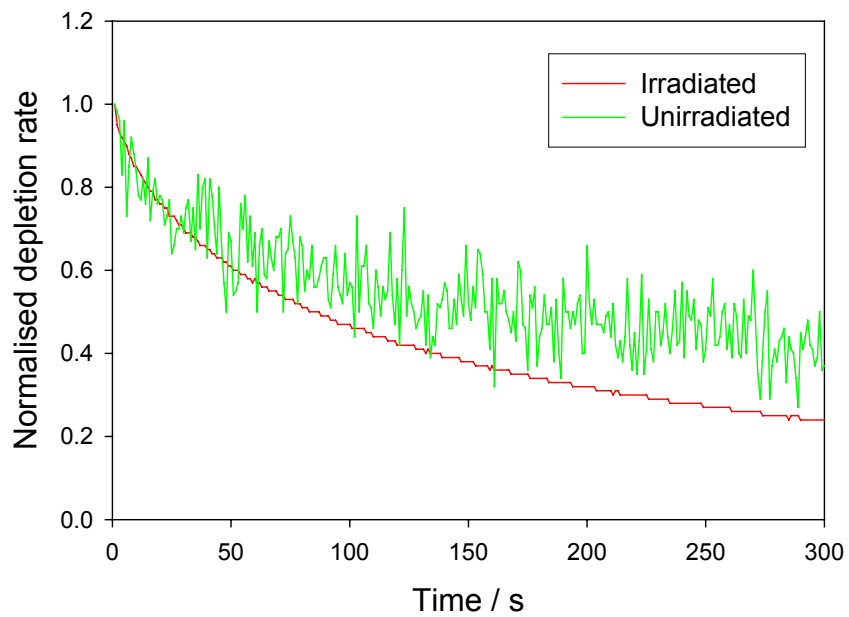
Fig 3.1 Mean and normalized depletion rate curves for SP12336 Dong quai

From Figures 3.1 (and Figures D.6-16) it can be seen that the general form of the curve for irradiated samples differs from that for unirradiated samples. This latter is almost flat, though that is partly an artefact of the graph scaling required to compare both curves on a single graph; this is demonstrated by the normalized curves which have similar shapes for the irradiated and unirradiated samples. It is also the case that the small magnitude of the unirradiated signal leads to much noisier curves.

3.1 Defining discriminant parameters from depletion rates

Some but not all curves display the expected faster depletion in the first 60 seconds (the normal measurement time) and this tends to be the case for both irradiation categories of a product. This implies that the nature of the product rather than its irradiation status determines the shape of the normalized depletion curve. In turn, this suggests that straightforward shape parameters will not be particularly useful in distinguishing the two types of sample and that un-normalized curves may be preferable. It may be advantageous to use curve-fitting approaches to overcome this. Two initial attempts have been made to parameterise the depletion characteristics. Immediately below the development of ratios of integrated PSL counts for successive 60 second sub-periods has been analysed. By taking the ratios of such signals from different parts of the curve it is possible to calculate scores both for each individual sample, and for the combined data sets which reflect the fractional reduction in signal level as the curves progress. Expressed in this way it is to be expected that unirradiated samples might show curves that deplete less, and therefore retain higher depletion ratios than recently irradiated signals that have not been exposed to light.

Figures 3.2 and 3.3 illustrate this approach by comparing depletion ratios calculated relative to the first 60 second integral for data near the beginning and at the end of the decay curves and also ratios relative to the 60-second interval preceding the interval used as the numerator. This simple approach seems to demonstrate the systematic differences in shapes between samples that had been irradiated, and those that were analysed untreated, as anticipated in the study design. One disadvantage of using a signal ratio is that it is ill-conditioned if the sample has no signal, and the values are subject to significant dispersion for data at the limit of photon counting statistics. The plots shown in figures 3.2 and 3.3 have been scaled to exclude outlying values where statistically limited counting data have led to such dispersed values. A further analysis of the data including development of propagated statistical uncertainties would be able to distinguish between points which fall beyond the loci for irradiated and unirradiated samples due to such measurement uncertainties. At present these plots look extremely promising and suggest that depletion rate analysis is worth pursuing further.
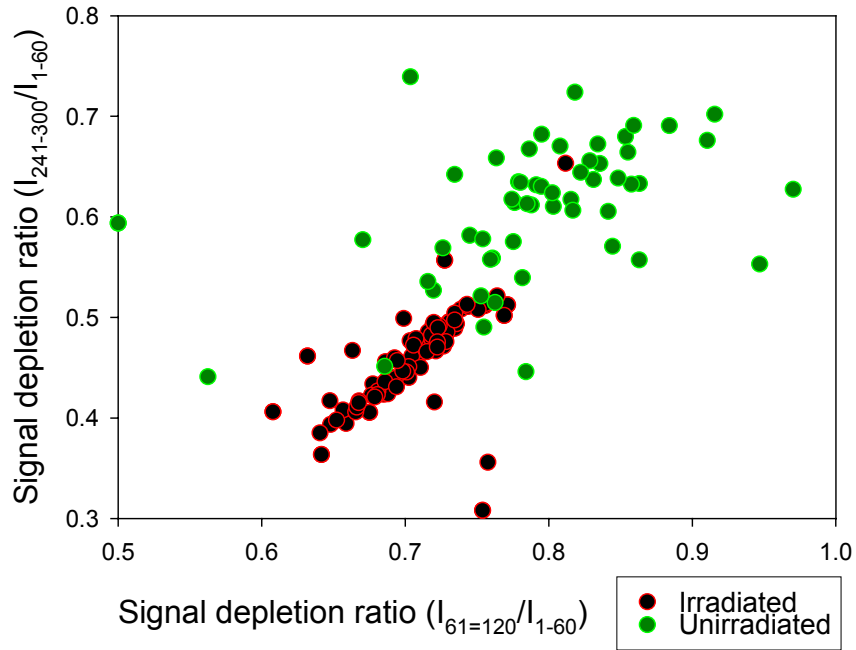
Figure 3.2 The surviving signal fractions from the second and last 60 second periods in the PSL decay curves normalised to the initial 60 second integral
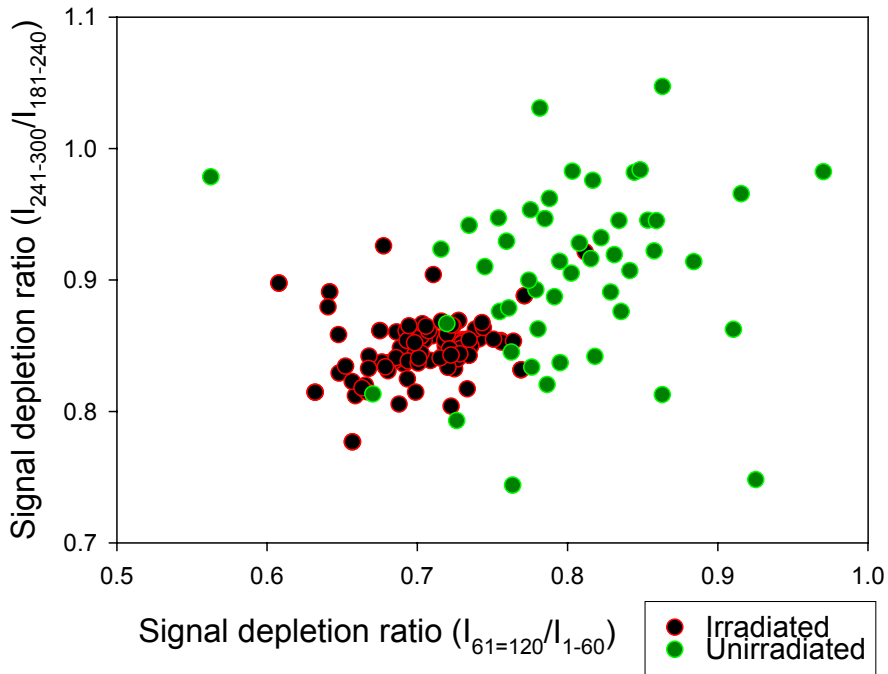
Figure 3.3 The surviving signal fractions from the second and last 60 second periods in the PSL decay curves normalised to the preceding 60 second integral

An alternative approach uses the ratio between the terminal count at 300 seconds and the count at 60 seconds taken from the data file.

	Siberian ginseng	Alfalfa	Green tea	Saw palmetto	Guarana	Milk thistle	Dandelion	Dong quai	Echinacea	*Gingko biloba*
Irradiated										
300/60 mean	2.80	3.15	3.21	5.79	2.96	2.95	3.24	2.99	3.21	3.18
SD	0.33	0.24	0.08	8.81	0.11	0.07	0.08	0.06	0.05	0.06
Unirradiated										
300/60 mean	1.24	3.62	2.31	1.64	3.26	3.32	3.24	3.34	1.82	3.47
SD	0.33	0.08	0.48	0.49	0.19	0.23	0.08	0.22	0.39	0.22

Table 3.1 Mean 300/60 second count ratios for irradiated and unirradiated products

From Table 3.1 it can be seen that the ratio for irradiated Saw palmetto is anomalous; this is due to the presence of a single outlier. Considering only the other products, there is no significant difference between irradiated and unirradiated samples either in the mean value or the spread of values. Therefore this ratio on its own cannot discriminate between irradiated and unirradiated material. It also implies that the difference in depletion rate seen graphically occurs in the first 60 seconds of measurement, a conclusion supported by examination of the graphs.

Nevertheless, it may be possible to define a discriminant parameter based on depletion rate *after* 60 seconds. Depletion after 60 seconds is very approximately linear, particularly for the normalised curves. This part of the curve can thus be considered to be the hypoteneuse (C) of a triangle with one side (A) of length 300-60 (i.e.240) and one side (B) of length [value at 60] – [value at 300]. It is thus possible to calculate an angle θ whose tangent is B/A. Such angles, calculated using mean depletion rates at 60 and 300 seconds for each product, are tabulated in Table 3.2. Tan θ represents the (negative) mean depletion acceleration during the period after the standard 60 second count has elapsed. For this table it can be seen that there is a marked difference in this parameter for irradiated and unirradiated samples. This is even the case for unirradiated alfalfa, which has already been seen to be unusual, although no evidence of an irradiated component was seen in the 10-fold replicate TL homogeneity testing performed for Project E01068. Siberian ginseng is also slightly anomalous, but the distinction between irradiated and unirradiated is still seen. Further work would be required to define a threshold value of θ.

Not normalised				Normalised			
Product	θ in degrees	Product	θ in degrees	Product	θ in degrees	Product	θ in degrees
SGI	8.16	SGU	0.91	SGI	0.08	SGU	-0.57
AlfI	89.90	AlfU	19.10	AlfI	0.08	AlfU	0.06
GTI	86.27	GTU	0.91	GTI	0.08	GTU	0.17
SPI	17.48	SPU	-0.64	SPI	0.05	SPU	1.29
GuaI	59.57	GuaU	0.72	GuaI	0.08	GuaU	0.02
MTI	80.71	MTU	8.39	MTI	0.08	MTU	0.07
DaI	89.92	DaU	6.82	DaI	0.08	DaU	0.07
DQI	89.80	DQU	4.81	DQI	0.08	DQU	0.08
EchI	87.66	EchU	-0.29	EchI	0.08	EchU	-0.13
GBI	89.77	GBU	2.65	GBI	0.10	GBU	0.04

Table 3.2 θ (arctangent mean depletion acceleration after 60 seconds) for all products

Figure 3.4 plots θ for irradiated and unirradiated products, in both normalised and non-normalised versions. The figure shows that there is almost complete separation of irradiated and unirradiated samples in the upper plot. Where there is less separation, it is the irradiated sample which is atypical. The lower, normalised, plot does not discriminate well.

θ for irradiated and unirradiated products
(not normalised)
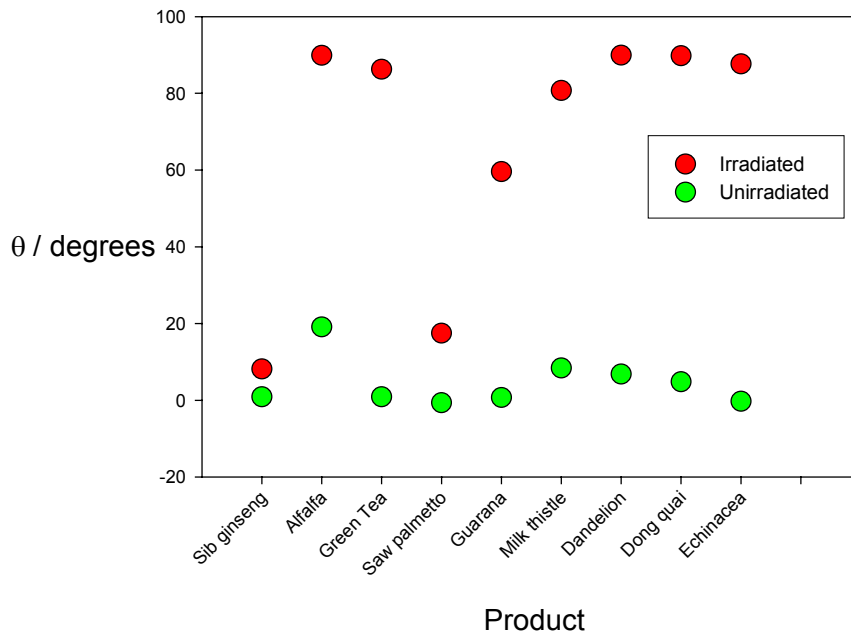
θ for irradiated and unirradiated products
(normalised)
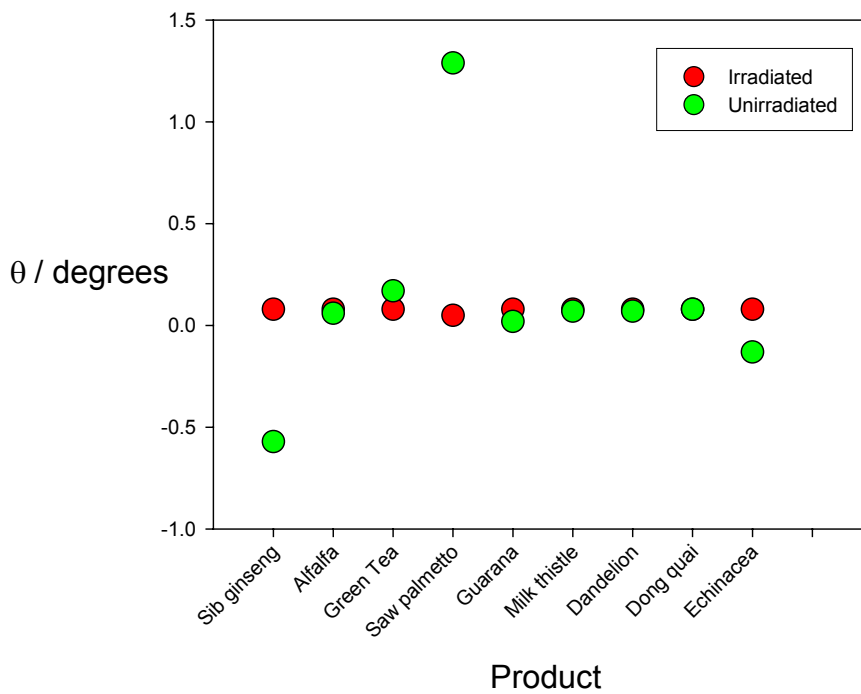
Figure 3.4 Arctangent of the deceleration of depletion rate for all products

3.2 Summary

Depletion rate analysis, including the use of calculated parameters, does provide a means of distinguishing irradiated from unirradiated samples, at least for those products examined here. Simple plots of the depletion rate, if results from irradiated and unirradiated portions of a product are plotted on the same scale, do not reveal enough detail in the unirradiated signal. It is therefore more promising to consider the ratios between different parts of the curves as described above.

Further work to refine this, and to examine samples which are known to give high PSL counts in the absence of low temperature TL signals (e.g. samples with high geological residuals) seems likely to yield results.

4. MULTIPLE WAVELENGTH STIMULATION

4.1 Background and method

Concentration methods have been shown above to improve in the detection of low sensitivity irradiated samples. These samples are characterised by low PSL in conjunction with positive TL. Other samples which display negative TL with intermediate or positive PSL present different challenges. In some cases the PSL signal derives from high mineral loads with significant geological residuals. Alternatively, the signal may be derived from water-soluble components or non-silicate phases which are removed during TL preparation. This section examines the possibility that the use of different stimulation wavelengths may help to discriminate between positive PSL derived from irradiated material and that derived from natural geological signals. Response to IRSL and OSL is a function of the mineralogy of the detrital grains in the sample, and may also be affected by the bleaching history of the material.

With the development of the SUERC Portable OSL Reader (Sanderson & Murphy, 2009) it has become possible to measure luminescence that has been stimulated by two different wavelengths using a single machine. Two versions of the portable equipment were available, one with continuous stimulation and one with pulsed stimulation.

These systems use the same detector head and sample drawer as the SUERC PPSL system used for the earlier experiments, with an adapted control box providing the choice of IRSL (880nm) and OSL (470nm) stimulation. The control box is operated manually and the stimulation sources can be switched on and off in conjunction with the counting software. The prototype OSL instrument delivers continuous wave (CW) stimulation whereas the second unit has pulsed stimulation control.

One set of experiments was conducted on the 10-fold replicates already measured with the single-wavelength instrument for 300 seconds (section 2.3.2), using continuous wave (CW) blue stimulation on the prototype OSL instrument. Measurements were conducted for 60 seconds.

A further set of measurements was performed using the second unit for both wavelengths, in pulsed mode. These samples were prepared in duplicate, using the 2-stage density separation method described above. Dark count measurement (10 seconds) were performed before and after stimulation at 880nm for 80 seconds, followed immediately by another 10-second dark count measurement, stimulation for 80 seconds at 470nm and a final 10-second dark count.

4.2 Results for 10-fold replicates

Table 4.1 presents red and blue measurements on the 10-fold replicates of all 10 products used in the depletion rate study that had pulsed PSL measurements previously carried out. From this it can be seen that the red measurements are consistently higher, often by an order of magnitude and sometimes almost by two. This may be caused by a combination of the mineralogy of the grains and of bleaching during the 300 second red measurement which preceded the blue. In general, the irradiated samples show a trend with a steeper

slope than the unirradiated samples, many of which show essentially no signal with either stimulation wavelength. Plots of these data can be found in Appendix D (Figures D.17-18).

	Siberian ginseng		Alfalfa		Green tea		Saw palmetto		Guarana	
Irradiated	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
red 60s	4580.20	3012.66	17512788.00	5155608.50	511892.70	224156.84	14315.20	6835.65	53522.00	37258.85
blue 60s	576.70	487.63	251562.70	155018.90	18274.30	13975.71	807.20	1003.25	1559.30	1834.51
red/blue	9.85	7.38	134.56	159.03	65.55	85.99	30.21	23.19	50.04	26.81

	Siberian ginseng		Alfalfa		Green tea		Saw palmetto		Guarana	
Unirradiated	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
red 60s	285.50	61.10	14667.50	2946.17	593.10	293.89	341.10	68.47	2555.20	1130.36
blue 60s	288.30	23.07	371.80	67.33	279.00	28.15	290.60	25.49	327.80	60.70
red/blue	0.99	0.19	40.66	10.84	2.14	1.08	1.19	0.30	7.98	3.84

	Milk thistle		Dandelion		Dong quai		Echinacea		*Gingko biloba*	
Irradiated	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
red 60s	190655.30	64103.09	23113484.50	3759105.37	8960559.20	2284500.74	818112.60	276125.03	6259060.40	1423244.77
blue 60s	1182.10	850.73	479614.40	334595.23	260381.50	80938.87	14042.60	8577.66	184075.90	71452.06
red/blue	228.61	140.81	65.97	30.14	36.30	10.04	87.57	66.47	38.38	15.87

	Milk thistle		Dandelion		Dong quai		Echinacea		Gingko biloba	
Unirradiated	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
red 60s	5619.50	3252.34	4717.40	2630.80	3055.00	2762.07	396.80	114.33	2603.00	1802.65
blue 60s	318.30	44.12	350.80	28.68	297.80	38.19	279.40	33.13	306.10	34.52
red/blue	18.20	11.22	13.45	7.19	9.71	7.20	1.42	0.36	8.58	5.75

Table 4.1 Red/blue measurements and ratios for 10-fold replication of all 10 products

Figure 4.1 plots the results for multiple stimulation of these samples and shows that, while there is some overlap between irradiated and unirradiated samples, the groups are broadly segregated and the trends are significantly different, with irradiated samples lying along a line similar to the calibrated PSL plots in Section 2. The unirradiated samples, however, do not display significant spread on the y-axis.
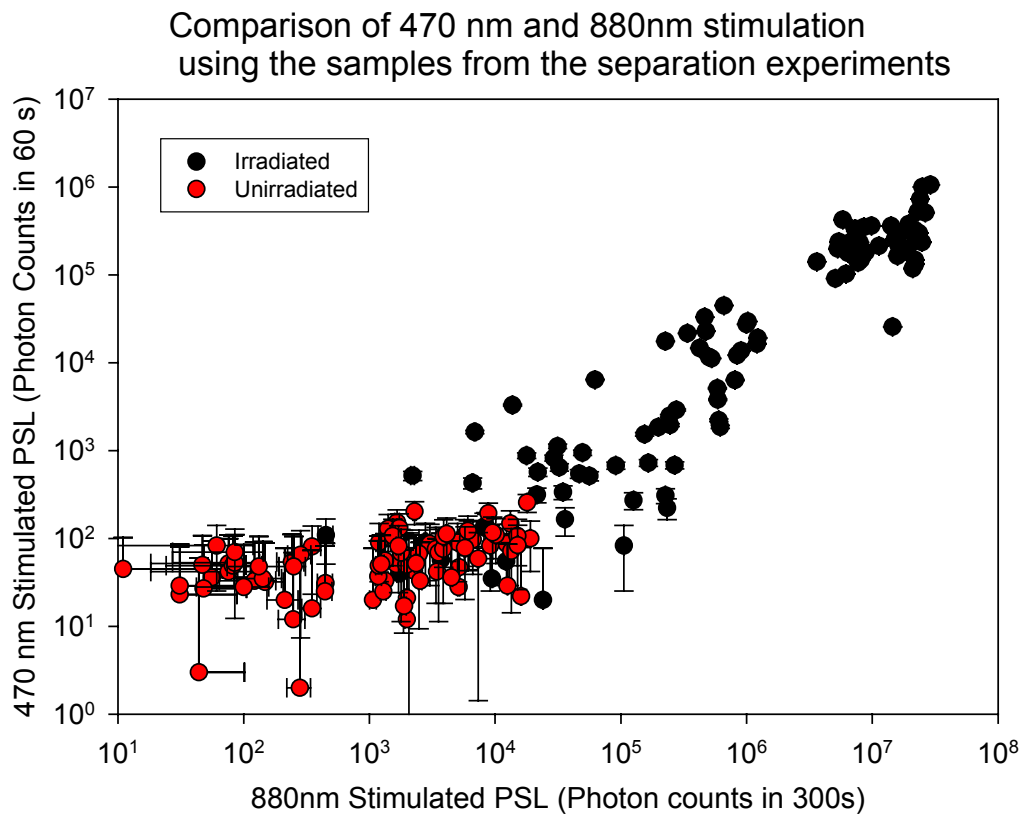
Figure 4.1 Wavelength comparison for the samples from the density separation experiments

4. 3   Results from combined red-blue measurements, 2-fold replication

In addition to the 10-fold replication described above, two further aliquots of each product in both irradiated and unirradiated form were taken through the density separation procedure. These separates were then measured in the IRSL/OSL system, using a 10-second dark count, red stimulation for 80 seconds, 20 seconds dark count, blue stimulation for 80 seconds, then a final 10-second dark count. The resulting data were then transferred into a spreadsheet. The spreadsheet calculates gross signal intensities for IRSL and OSL, their statistical uncertainties, the interpolated background ratios of the instrument before and after measurement and the net IRSL and OSL signals after background subtraction. The red/blue ratio is also calculated. These calculated parameters are presented in Appendix E.

Figure 4.2 Gross IRSL/OSL counts for the 10 samples with 2-fold replication

Figure 4.2 shows gross IRSL and OSL intensitiesthat stimulation wavelength does not affect ability to distinguish irradiated and unirradiated samples; the two categories are separated by signal intesities at both wavelengths.

Figure 4.3 Net IRSL/OSL counts for the 10 samples with 2-fold replication

Figure 4.3 shows the net signal for both stimulation wavelengths; background subtraction results in negative terminal counts for some of the least sensitive unirradiated samples. However the same relation ship is evident.

Comparison of 470 nm and 880nm stimulation
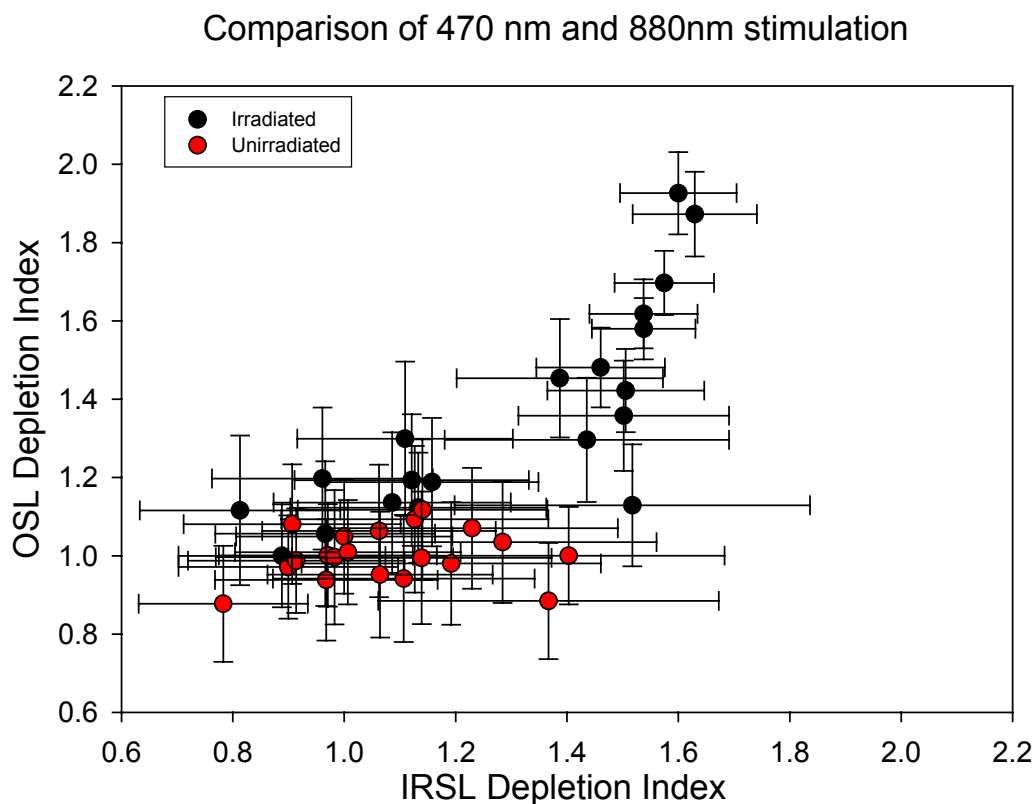
Figure 4.4 IRSL/OSL Depletion index plot for the 10 samples with 2-fold replication

Figure 4.4 shows the IRSL/OSL depletion index for the 10 samples with 2-fold replication. Depletion index is the ratio between the cumulative count for the first half of the measurement period and the cumulative count for the second half. For the unirradiated samples, the OSL depletion index is approximately 1, indicating a constant rate of luminescence emission or system background at very low signal levels. The IRSL depletion index has a spread of 0.8 - 1.4, showing that although there is depletion, this is not large. For the irradiated samples, depletion index for both IRSL and OSL shows a much greater variation. For some irradiated samples, there is a high depletion index for both the IRSL and OSL. Even those irradiated samples which show the lowest OSL depletion indices can still be distinguished from unirradiated samples. Comparison IRSL depletion indices reinforces the conclusions of the depletion rate analysis described in section 3.

4.4 Summary

The use of multiple wavelength stimulation on both previously measured and freshly prepared material shows that irradiated and unirradiated material can be distinguished by signal intensity at both wavelengths tested. Depletion index, which depends on the rate at which the signal is emitted in response to stimulation, does vary with wavelength, however. This suggests that shorter wavelength stimulation than that employed in the standard pulsed PSL system may be useful in discriminating between low sensitivity irradiated material and unirradiated samples when coupled to an analysis of depletion rate. The technique is easy to perform with the recently developed portable OSL equipment. A further series of investigations, with samples known to have high geological residuals, would be worth conducting. It might also be worth assessing whether the additional sample preparation steps introduced to enhance sensitivity are necessary when a different problem is being addressed; discrimination might be possible with the whole samples used in standard PSL procedure (EN13751), enabling faster testing.

5. DISCUSSION and CONCLUSIONS

This report presents data from a sequence of experiments designed to investigate the potential for enhancing PSL signals by expanding sample preparation. An assessment of the potential for this can be made straightforwardly by comparing PSL terminal counts before and after the additional steps. It is clear from the data presented above that protocols which include a density separation are more likely to enhance signals due to low sensitivity than simple settling, but that there are also differences in behaviour between irradiated and unirradiated material which may affect the efficiency of the extra steps.

At this stage there was no investigation of the effect of varying tungstate density (2.0 should separate organic matter from minerals but it may be possible to achieve an equally good results with a lower density) which has implications for cost and recycling. Other heavy liquids, including disposable ones, may also be adequate although care has to be taken not to trigger precipitation. The use of non-aqueous solvents when dealing with plant extracts also requires further work.

It is also possible to use all the data collected during an extended 300-second PSL measurement to examine depletion rate with a view to defining one or more parameters which can discriminate between irradiated and unirradiated material. Initial work shows promise, but it is likely that refinements of the techniques would enhance this discriminatory function. It appears to be necessary to extend the measurement period beyond the usual 60 seconds stipulated by EN13751. This is the case whether integrals from different parts of the depletion curve are compared or a parameter calculated from the curve beyond the normal measurement period.

In addition, the use of multiple wavelength stimulation has been explored; the experiments performed on these particular samples do not suggest that this either the blue or infra-red wavelength adds a great deal of information. However the use of the blue depletion index shows some promising initial results with a small discrimination between the unirradiated and low sensitive irradiated samples. Further work it may be found that there are some classes of sample for which it is appropriate.

Optical and scanning electron microscopy have been performed on a small subset of the separated samples; an extension of this investigation might demonstrate whether there is a consistent difference in the minerals separated by the two methods (mineralogy, particle size, presence of organic matter after the separation process).

Deciding to use an enhanced technique in cases where initial PSL is not negative will depend partly on prior knowledge of sample types where sensitivity is likely to be low; calibrated PSL can also be introduced as a means of selecting samples of unknown sensitivity for expanded sample preparation.

From the above results, it is clear that although some progress has been made towards reducing the incidence of PSL classifications which would not be corroborated by TL analysis performed on the same material, there is still scope for further investigation.

In particular, extension of the techniques already to examined to other matrices, such as a wider range of extracts, and to finished products in powder, capsules and tablet form (for instance) might lead to a different decision tree (see Appendix C) including additional

options. Examination of material known to contain irradiated components in an unirradiated bulk, including those of low sensitivity, could delimit the discriminatory power associated with each technique.

For depletion rate analysis and red/blue stimulation, additional study materials including those known to produce high PSL signals in the absence of observable low temperature TL need to be used to assess the usefulness of the proposed parameters. Such study is likely to require the purchase of more material in order to obtain sufficient quantities to perform analysis at a significant level of replication.

Overall, therefore, it can be concluded that this has been a useful exploratory study which has shown that some enhancement of PSL signal is possible in most cases if steps from the TL procedure are added to the normal PSL screening protocol. Deciding whether this might be a helpful approach probably requires prior recourse to calibrated PSL. It is then better to use a heavy liquid if low sensitivity is the problem; depletion rate analysis can help to identify irradiated materials and the use OSL multi-wavelength stimulation has shown some promising results for low sensitivity irradiated samples.

Further work is needed to refine the techniques but all enhancements will necessitate some extra work for the analyst, with depletion rate analysis requiring the least since the number of measurement cycles only needs to be enlarged and then all the data are ready for examination.

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Also need acknowledgments and tables of figures etc. at the beginning and possibly a summary there too.

Appendix A PPSL data for settling and density separation experiments

PPSL data for settling and density separation experiments for 10-fold replication of 10 products, with red/blue ratios for the density separation samples

Infra-Red measurements conducted on SUERC PPSL instrument
Blue measurements conducted on SUERC SPOR instrument

PSL1A	Initial terminal count for settling method
PSL2A	Terminal count after settling protocol applied
PSL1B	Initial terminal count for density separation method
300s	Terminal count after density separation
PSL2B	Count at 60 seconds after density separation
300/60	Ratio between terminal count at 300s and count at 60s (density separated samples only)
CF	Ratio between PSL2A and PSL1A or PSL2B and PSL2A
Red/blue	Ratio between red counts at 60s and separate blue measurement of same samples for 60s

Irradiated

Aliquot	1	2	3	4	5	6	7	8	9	10	Mean	SD
PSL1A	449	501	473	359	427	846	389	416	501	523	488.40	136.14
PSL2A	1683	635	556	955	640	1278	623	1220	940	1854	1038.40	461.21
CF	3.75	1.27	1.18	2.66	1.50	1.51	1.60	2.93	1.88	3.54	2.18	0.96
PSL1B	500	449	314	547	806	413	687	418	494	432	506.00	143.99
PSL2B	3043	7151	3959	2123	8683	2463	6868	8822	707	1983	4580.20	3012.66
300s	8201	23254	11396	5026	24379	6688	22453	24239	1609	5940	13318.50	9176.74
blue 60s	347	1884	313	322	395	775	684	386	365	296	576.70	487.63
red/blue	8.77	3.80	12.65	6.59	21.98	3.18	10.04	22.85	1.94	6.70	9.85	7.38

Unirradiated

Aliquot	1	2	3	4	5	6	7	8	9	10	Mean	SD
PSL1A	312	272	202	279	270	319	279	260	330	277	280.00	36.06
PSL2A	317	295	300	327	224	231	301	248	338	298	287.90	39.82
CF	1.02	1.08	1.49	1.17	0.83	0.72	1.08	0.95	1.02	1.08	1.04	0.20
PSL1B	274	322	459	300	317	258	295	263	404	253	314.50	67.34
PSL2B	404	224	312	197	267	332	255	245	287	332	285.50	61.10
300s	602	319	416	298	141	467	356	181	395	398	357.30	133.87
blue 60s	288	309	292	240	301	308	309	259	279	298	288.30	23.07
red/blue	1.40	0.72	1.07	0.82	0.89	1.08	0.83	0.95	1.03	1.11	0.99	0.19

Log10

Irradiated

Aliquot	1	2	3	4	5	6	7	8	9	10	Mean	SD
PSL1A	2.65	2.70	2.67	2.56	2.63	2.93	2.59	2.62	2.70	2.72	2.68	0.10
PSL2A	3.23	2.80	2.75	2.98	2.81	3.11	2.79	3.09	2.97	3.27	2.98	0.19
CF	0.57	0.10	0.07	0.42	0.18	0.18	0.20	0.47	0.27	0.55	0.30	0.19
PSL1B	2.70	2.65	2.50	2.74	2.91	2.62	2.84	2.62	2.69	2.64	2.69	0.12
PSL2B	3.48	3.85	3.60	3.33	3.94	3.39	3.84	3.95	2.85	3.30	3.55	0.35
300s	3.91	4.37	4.06	3.70	4.39	3.83	4.35	4.38	3.21	3.77	4.00	0.39
blue 60s	2.54	3.28	2.50	2.51	2.60	2.89	2.84	2.59	2.56	2.47	2.68	0.25
red/blue	0.94	0.58	1.10	0.82	1.34	0.50	1.00	1.36	0.29	0.83	0.88	0.35

Unirradiated

Aliquot	1	2	3	4	5	6	7	8	9	10	Mean	SD
PSL1A	2.49	2.43	2.31	2.45	2.43	2.50	2.45	2.41	2.52	2.44	2.44	0.06
PSL2A	2.50	2.47	2.48	2.51	2.35	2.36	2.48	2.39	2.53	2.47	2.46	0.06
CF	0.01	0.04	0.17	0.07	-0.08	-0.14	0.03	-0.02	0.01	0.03	0.01	0.08
PSL1B	2.44	2.51	2.66	2.48	2.50	2.41	2.47	2.42	2.61	2.40	2.49	0.09
PSL2B	2.61	2.35	2.49	2.29	2.43	2.52	2.41	2.39	2.46	2.52	2.45	0.09
300s	2.78	2.50	2.62	2.47	2.15	2.67	2.55	2.26	2.60	2.60	2.52	0.19
blue 60s	2.46	2.49	2.47	2.38	2.48	2.49	2.49	2.41	2.45	2.47	2.46	0.04
red/blue	0.15	-0.14	0.03	-0.09	-0.05	0.03	-0.08	-0.02	0.01	0.05	-0.01	0.08

log CF and log 300/60 are the logs of the quotients, not the quotients of the logs

Table A.1 PPSL data for SP10950 Siberian ginseng

A. 2

Irradiated

Aliquot	1	2	3	4	5	6	7	8	9	10	Mean	SD
PSL1A	2242168	2099639	2218939	2022180	2174403	2355715	2184084	1961760	2177410	2172313	2160861.10	111405.88
PSL2A	4810260	6967246	6191405	3988265	6980949	11067215	6029221	2164011	5646085	10023641	6386829.80	2637505.63
CF	2.15	3.32	2.79	1.97	3.21	4.70	2.76	1.10	2.59	4.61	2.92	1.12
PSL1B	1880880	2261595	2346071	2079649	2229149	2020113	2291655	1783683	1887443	1958944	2073918.20	198106.53
PSL2B	19458412	23072315	14479870	5814317	15165584	21836832	16170726	16290063	20949546	21890215	17512788.00	5155608.50
300s	56189206	72654297	43018337	22024409	46438237	69514693	50749735	49994371	64902551	69170266	54465610.20	15517519.37
blue 60s	378406	524599	25929	424392	256595	148776	216912	288324	118506	133188	251562.70	155018.90
red/blue	51.42	43.98	558.44	13.70	59.10	146.78	74.55	56.50	176.78	164.36	134.56	159.03

Unirradiated

Aliquot	1	2	3	4	5	6	7	8	9	10	Mean	SD
PSL1A	2669	1973	1732	1765	2110	1914	1774	1963	2112	1626	1963.80	295.63
PSL2A	5350	6942	2153	3191	2390	4777	2509	3819	4115	3818	3906.40	1489.00
CF	2.00	3.52	1.24	1.81	1.13	2.50	1.41	1.95	1.95	2.35	1.99	0.70
PSL1B	1777	1641	1630	1671	1918	1677	1891	1673	1932	1485	1729.50	145.97
PSL2B	16348	9094	13232	12587	19338	13467	15304	13701	18240	15364	14667.50	2946.17
300s	57472	32583	48013	45864	72471	47132	54941	51096	67161	55441	53217.40	11252.71
blue 60s	278	450	343	343	356	404	363	328	513	340	371.80	67.33
red/blue	58.81	20.21	38.58	36.70	54.32	33.33	42.16	41.77	35.56	45.19	40.66	10.84

Log10

Irradiated

Aliquot	1	2	3	4	5	6	7	8	9	10	Mean	SD
PSL1A	6.35	6.32	6.35	6.31	6.34	6.37	6.34	6.29	6.34	6.34	6.33	0.02
PSL2A	6.68	6.84	6.79	6.60	6.84	7.04	6.78	6.34	6.75	7.00	6.77	0.20
CF	0.33	0.52	0.45	0.29	0.51	0.67	0.44	0.04	0.41	0.66	0.43	0.18
PSL1B	6.27	6.35	6.37	6.32	6.35	6.31	6.36	6.25	6.28	6.29	6.31	0.04
PSL2B	7.29	7.36	7.16	6.76	7.18	7.34	7.21	7.21	7.32	7.34	7.22	0.18
300s	7.75	7.86	7.63	7.34	7.67	7.84	7.71	7.70	7.81	7.84	7.72	0.15
blue 60s	5.58	5.72	4.41	5.63	5.41	5.17	5.34	5.46	5.07	5.12	5.29	0.38
red/blue	1.71	1.64	2.75	1.14	1.77	2.17	1.87	1.75	2.25	2.22	1.93	0.44

Unirradiated

Aliquot	1	2	3	4	5	6	7	8	9	10	Mean	SD
PSL1A	3.43	3.30	3.24	3.25	3.32	3.28	3.25	3.29	3.32	3.21	3.29	0.06
PSL2A	3.73	3.84	3.33	3.50	3.38	3.68	3.40	3.58	3.61	3.58	3.56	0.16
CF	0.30	0.55	0.09	0.26	0.05	0.40	0.15	0.29	0.29	0.37	0.28	0.15
PSL1B	3.25	3.22	3.21	3.22	3.28	3.22	3.28	3.22	3.29	3.17	3.24	0.04
PSL2B	4.21	3.96	4.12	4.10	4.29	4.13	4.18	4.14	4.26	4.19	4.16	0.09
300s	4.76	4.51	4.68	4.66	4.86	4.67	4.74	4.71	4.83	4.74	4.72	0.10
blue 60s	2.44	2.65	2.54	2.54	2.55	2.61	2.56	2.52	2.71	2.53	2.56	0.08
red/blue	1.77	1.31	1.59	1.56	1.73	1.52	1.62	1.62	1.55	1.66	1.59	0.13

log CF and log 300/60 are the logs of the quotients, not the quotients of the logs

Table A.2 PPSL data for SP10951 Alfalfa

A. 3

Irradiated

Aliquot	1	2	3	4	5	6	7	8	9	10	Mean	SD
PSL1A	46682	51792	36991	45319	23296	31645	38027	45369	55559	64621	43930.10	12001.92
PSL2A	362864	430132	69242	58572	350863	140931	397201	62306	224823	207666	230460.00	146089.19
CF	7.77	8.30	1.87	1.29	15.06	4.45	10.45	1.37	4.05	3.21	5.78	4.53
PSL1B	51213	41179	48550	52347	31984	36514	45356	31968	31058	36733	40690.20	8220.23
PSL2B	276846	617066	464584	423625	998324	585793	660267	527368	338788	226266	511892.70	224156.84
300s	851988	1912354	1480924	1343295	3285681	1882021	2138993	1732065	1115665	726567	1646955.30	740989.73
blue 60s	3154	2118	33285	14926	27704	5371	45040	11449	21891	17805	18274.30	13975.71
red/blue	87.78	291.34	13.96	28.38	36.04	109.07	14.66	46.06	15.48	12.71	65.55	85.99

Unirradiated

PSL1A	462	443	469	501	438	524	550	466	668	490	501.10	68.35
PSL2A	386	336	364	349	293	399	302	342	350	286	340.70	37.92
CF	0.84	0.76	0.78	0.70	0.67	0.76	0.55	0.73	0.52	0.58	0.69	0.11
PSL1B	437	517	465	427	444	414	574	436	486	436	463.60	49.39
PSL2B	703	295	711	606	468	287	504	498	536	1323	593.10	293.89
300s	1604	707	2091	1560	942	635	797	936	1117	4211	1460.00	1072.10
blue 60s	287	244	249	337	276	285	268	310	258	276	279.00	28.15
red/blue	2.45	1.21	2.86	1.80	1.70	1.01	1.88	1.61	2.08	4.79	2.14	1.08

Log10

Irradiated

Aliquot	1	2	3	4	5	6	7	8	9	10	Mean	SD
PSL1A	4.67	4.71	4.57	4.66	4.37	4.50	4.58	4.66	4.74	4.81	4.63	0.13
PSL2A	5.56	5.63	4.84	4.77	5.55	5.15	5.60	4.79	5.35	5.32	5.26	0.35
CF	0.89	0.92	0.27	0.11	1.18	0.65	1.02	0.14	0.61	0.51	0.63	0.37
PSL1B	4.71	4.61	4.69	4.72	4.50	4.56	4.66	4.50	4.49	4.57	4.60	0.09
PSL2B	5.44	5.79	5.67	5.63	6.00	5.77	5.82	5.72	5.53	5.35	5.67	0.19
300s	5.93	6.28	6.17	6.13	6.52	6.27	6.33	6.24	6.05	5.86	6.18	0.20
blue 60s	3.50	3.33	4.52	4.17	4.44	3.73	4.65	4.06	4.34	4.25	4.10	0.45
red/blue	1.94	2.46	1.14	1.45	1.56	2.04	1.17	1.66	1.19	1.10	1.57	0.46

Unirradiated

PSL1A	2.66	2.65	2.67	2.70	2.64	2.72	2.74	2.67	2.82	2.69	2.70	0.05
PSL2A	2.59	2.53	2.56	2.54	2.47	2.60	2.48	2.53	2.54	2.46	2.53	0.05
CF	-0.08	-0.12	-0.11	-0.16	-0.17	-0.12	-0.26	-0.13	-0.28	-0.23	-0.17	0.07
PSL1B	2.64	2.71	2.67	2.63	2.65	2.62	2.76	2.64	2.69	2.64	2.66	0.04
PSL2B	2.85	2.47	2.85	2.78	2.67	2.46	2.70	2.70	2.73	3.12	2.73	0.19
300s	3.21	2.85	3.32	3.19	2.97	2.80	2.90	2.97	3.05	3.62	3.09	0.25
blue 60s	2.46	2.39	2.40	2.53	2.44	2.45	2.43	2.49	2.41	2.44	2.44	0.04
red/blue	0.39	0.08	0.46	0.25	0.23	0.00	0.27	0.21	0.32	0.68	0.29	0.19

log CF and log 300/60 are the logs of the quotients, not the quotients of the logs

Table A.3 PPSL data for SP10952 Green tea

Irradiated

Aliquot	1	2	3	4	5	6	7	8	9	10	Mean	SD
PSL1A	1863	1382	1514	1686	1332	2772	1520	1954	1319	1155	1649.70	466.77
PSL2A	878	2479	830	744	563	12639	1032	4165	4567	597	2849.40	3751.38
CF	0.47	1.79	0.55	0.44	0.42	4.56	0.68	2.13	3.46	0.52	1.50	1.48
PSL1B	3279	1170	2096	2928	1117	1848	2179	2244	1642	1297	1980.00	723.26
PSL2B	12497	21734	18043	24305	22075	14002	8413	6452	5941	9690	14315.20	6835.65
300s	36284	66889	51150	75194	66755	432191	25061	19293	18461	29152	82043.00	124805.09
blue 60s	311	571	1134	276	826	3551	392	358	362	291	807.20	1003.25
red/blue	40.18	38.06	15.91	88.06	26.73	3.94	21.46	18.02	16.41	33.30	30.21	23.19

Unirradiated

Aliquot	1	2	3	4	5	6	7	8	9	10	Mean	SD
PSL1A	285	275	367	397	309	262	343	512	265	244	325.90	82.14
PSL2A	326	262	375	335	293	503	217	306	227	327	317.10	81.84
CF	1.14	0.95	1.02	0.84	0.95	1.92	0.63	0.60	0.86	1.34	1.03	0.38
PSL1B	254	282	239	341	286	305	228	234	260	278	270.70	35.12
PSL2B	300	241	304	491	317	303	378	338	398	341	341.10	68.47
300s	360	290	752	976	346	613	765	371	711	503	568.70	229.60
blue 60s	259	269	283	256	339	306	289	305	291	309	290.60	25.49
red/blue	1.16	0.90	1.07	1.92	0.94	0.99	1.31	1.11	1.37	1.10	1.19	0.30

Log10

Irradiated

Aliquot	1	2	3	4	5	6	7	8	9	10	Mean	SD
PSL1A	3.27	3.14	3.18	3.23	3.12	3.44	3.18	3.29	3.12	3.06	3.20	0.11
PSL2A	2.94	3.39	2.92	2.87	2.75	4.10	3.01	3.62	3.66	2.78	3.20	0.46
CF	-0.33	0.25	-0.26	-0.36	-0.37	0.66	-0.17	0.33	0.54	-0.29	0.00	0.40
PSL1B	3.52	3.07	3.32	3.47	3.05	3.27	3.34	3.35	3.22	3.11	3.27	0.16
PSL2B	4.10	4.34	4.26	4.39	4.34	4.15	3.92	3.81	3.77	3.99	4.11	0.23
300s	4.56	4.83	4.71	4.88	4.82	5.64	4.40	4.29	4.27	4.46	4.68	0.40
blue 60s	2.49	2.76	3.05	2.44	2.92	3.55	2.59	2.55	2.56	2.46	2.74	0.35
red/blue	1.60	1.58	1.20	1.94	1.43	0.60	1.33	1.26	1.22	1.52	1.37	0.35

Unirradiated

Aliquot	1	2	3	4	5	6	7	8	9	10	Mean	SD
PSL1A	2.45	2.44	2.56	2.60	2.49	2.42	2.54	2.71	2.42	2.39	2.50	0.10
PSL2A	2.51	2.42	2.57	2.53	2.47	2.70	2.34	2.49	2.36	2.51	2.49	0.11
CF	0.06	-0.02	0.01	-0.07	-0.02	0.28	-0.20	-0.22	-0.07	0.13	-0.01	0.15
PSL1B	2.40	2.45	2.38	2.53	2.46	2.48	2.36	2.37	2.41	2.44	2.43	0.05
PSL2B	2.48	2.38	2.48	2.69	2.50	2.48	2.58	2.53	2.60	2.53	2.53	0.08
300s	2.56	2.46	2.88	2.99	2.54	2.79	2.88	2.57	2.85	2.70	2.72	0.18
blue 60s	2.41	2.43	2.45	2.41	2.53	2.49	2.46	2.48	2.46	2.49	2.46	0.04
red/blue	0.06	-0.05	0.03	0.28	-0.03	0.00	0.12	0.04	0.14	0.04	0.06	0.10

log CF and log 300/60 are the logs of the quotients, not the quotients of the logs

Table A.4 PPSL data for SP10953 Saw palmetto

Irradiated

Aliquot	1	2	3	4	5	6	7	8	9	10	Mean	SD
PSL1A	18687	12149	20401	11369	38072	16198	10958	14851	34245	13421	19035.10	9569.82
PSL2A	22638	24539	5550	9003	65657	25730	9502	7350	10595	23347	20391.10	17773.42
CF	1.21	2.02	0.27	0.79	1.72	1.59	0.87	0.49	0.31	1.74	1.10	0.64
PSL1B	17225	12155	14237	9644	14132	7943	10191	16306	18232	10288	13035.30	3523.71
PSL2B	56465	154575	32635	31637	62512	29577	34895	49764	36199	46961	53522.00	37258.85
300s	161457	429939	98991	92355	191080	84755	102614	153551	111626	141102	156747.00	102046.29
blue 60s	770	1790	903	1375	6657	1079	593	1204	421	801	1559.30	1834.51
red/blue	73.33	86.35	36.14	23.01	9.39	27.41	58.84	41.33	85.98	58.63	50.04	26.81

Unirradiated

Aliquot	1	2	3	4	5	6	7	8	9	10	Mean	SD
PSL1A	314	523	528	504	439	722	439	601	429	423	492.20	112.16
PSL2A	499	1011	268	348	298	562	307	414	252	352	431.10	226.88
CF	1.59	1.93	0.51	0.69	0.68	0.78	0.70	0.69	0.59	0.83	0.90	0.47
PSL1B	367	472	874	401	500	468	436	541	639	432	513.00	148.03
PSL2B	2153	2540	2521	1916	2318	5436	3285	1594	2243	1546	2555.20	1130.36
300s	6907	8381	8174	5890	6780	19129	11239	5055	7863	5043	8446.10	4178.01
blue 60s	313	459	299	409	314	303	343	289	268	281	327.80	60.70
red/blue	6.88	5.53	8.43	4.68	7.38	17.94	9.58	5.52	8.37	5.50	7.98	3.84

Log10

Irradiated

Aliquot	1	2	3	4	5	6	7	8	9	10	Mean	SD
PSL1A	4.27	4.08	4.31	4.06	4.58	4.21	4.04	4.17	4.53	4.13	4.24	0.19
PSL2A	4.35	4.39	3.74	3.95	4.82	4.41	3.98	3.87	4.03	4.37	4.19	0.33
CF	0.08	0.31	-0.57	-0.10	0.24	0.20	-0.06	-0.31	-0.51	0.24	-0.05	0.32
PSL1B	4.24	4.08	4.15	3.98	4.15	3.90	4.01	4.21	4.26	4.01	4.10	0.12
PSL2B	4.75	5.19	4.51	4.50	4.80	4.47	4.54	4.70	4.56	4.67	4.67	0.21
300s	5.21	5.63	5.00	4.97	5.28	4.93	5.01	5.19	5.05	5.15	5.14	0.21
blue 60s	2.89	3.25	2.96	3.14	3.82	3.03	2.77	3.08	2.62	2.90	3.05	0.33
red/blue	1.87	1.94	1.56	1.36	0.97	1.44	1.77	1.62	1.93	1.77	1.62	0.30

Unirradiated

Aliquot	1	2	3	4	5	6	7	8	9	10	Mean	SD
PSL1A	2.50	2.72	2.72	2.70	2.64	2.86	2.64	2.78	2.63	2.63	2.68	0.10
PSL2A	2.70	3.00	2.43	2.54	2.47	2.75	2.49	2.62	2.40	2.55	2.59	0.18
CF	0.20	0.29	-0.29	-0.16	-0.17	-0.11	-0.16	-0.16	-0.23	-0.08	-0.09	0.19
PSL1B	2.56	2.67	2.94	2.60	2.70	2.67	2.64	2.73	2.81	2.64	2.70	0.11
PSL2B	3.33	3.40	3.40	3.28	3.37	3.74	3.52	3.20	3.35	3.19	3.38	0.16
300s	3.84	3.92	3.91	3.77	3.83	4.28	4.05	3.70	3.90	3.70	3.89	0.17
blue 60s	2.50	2.66	2.48	2.61	2.50	2.48	2.54	2.46	2.43	2.45	2.51	0.07
red/blue	0.84	0.74	0.93	0.67	0.87	1.25	0.98	0.74	0.92	0.74	0.87	0.17

log CF and log 300/60 are the logs of the quotients, not the quotients of the logs

Table A.5 PPSL data for SP10954 Guarana

Irradiated

Aliquot	1	2	3	4	5	6	7	8	9	10	Mean	SD
PSL1A	118882	134100	151952	150729	113749	103247	142303	139432	114841	103741	127297.60	18614.35
PSL2A	46178	85596	70217	36885	24829	34059	41431	34520	28209	24571	42649.50	20122.82
CF	0.39	0.64	0.46	0.24	0.22	0.33	0.29	0.25	0.25	0.24	0.33	0.13
PSL1B	139097	148367	167686	133996	131817	125695	106005	106577	115014	116084	129033.80	19469.17
PSL2B	244107	226246	268045	246739	233264	91287	126318	105846	165541	199160	190655.30	64103.09
300s	698037	682082	800536	749244	707238	274972	361535	305928	480408	581671	564165.10	194685.23
blue 60s	2741	565	939	2211	479	934	528	339	981	2104	1182.10	850.73
red/blue	89.06	400.44	285.46	111.60	486.98	97.74	239.24	312.23	168.75	94.66	228.61	140.81

Unirradiated

Aliquot	1	2	3	4	5	6	7	8	9	10	Mean	SD
PSL1A	4163	1533	3117	2586	4644	3049	2586	3346	3484	2689	3119.70	873.92
PSL2A	401	536	429	825	336	1348	1140	340	599	401	635.50	355.74
CF	0.10	0.35	0.14	0.32	0.07	0.44	0.44	0.10	0.17	0.15	0.23	0.15
PSL1B	3081	3387	2610	2519	2787	3401	10439	3184	1889	7015	4031.20	2642.38
PSL2B	4160	3637	5386	9412	3706	5279	12794	6348	1665	3808	5619.50	3252.34
300s	11734	12949	17401	30323	13053	18877	41734	21469	5274	13040	18585.40	10544.59
blue 60s	232	332	284	339	298	346	285	357	385	325	318.30	44.12
red/blue	17.93	10.95	18.96	27.76	12.44	15.26	44.89	17.78	4.32	11.72	18.20	11.22

Log10

Irradiated

Aliquot	1	2	3	4	5	6	7	8	9	10	Mean	SD
PSL1A	5.08	5.13	5.18	5.18	5.06	5.01	5.15	5.14	5.06	5.02	5.10	0.06
PSL2A	4.66	4.93	4.85	4.57	4.39	4.53	4.62	4.54	4.45	4.39	4.59	0.18
CF	-0.41	-0.19	-0.34	-0.61	-0.66	-0.48	-0.54	-0.61	-0.61	-0.63	-0.51	0.15
PSL1B	5.14	5.17	5.22	5.13	5.12	5.10	5.03	5.03	5.06	5.06	5.11	0.06
PSL2B	5.39	5.35	5.43	5.39	5.37	4.96	5.10	5.02	5.22	5.30	5.25	0.17
300s	5.84	5.83	5.90	5.87	5.85	5.44	5.56	5.49	5.68	5.76	5.72	0.17
blue 60s	3.44	2.75	2.97	3.34	2.68	2.97	2.72	2.53	2.99	3.32	2.97	0.31
red/blue	1.95	2.60	2.46	2.05	2.69	1.99	2.38	2.49	2.23	1.98	2.28	0.28

Unirradiated

Aliquot	1	2	3	4	5	6	7	8	9	10	Mean	SD
PSL1A	3.62	3.19	3.49	3.41	3.67	3.48	3.41	3.52	3.54	3.43	3.48	0.13
PSL2A	2.60	2.73	2.63	2.92	2.53	3.13	3.06	2.53	2.78	2.60	2.75	0.22
CF	-1.02	-0.46	-0.86	-0.50	-1.14	-0.35	-0.36	-0.99	-0.76	-0.83	-0.73	0.29
PSL1B	3.49	3.53	3.42	3.40	3.45	3.53	4.02	3.50	3.28	3.85	3.55	0.22
PSL2B	3.62	3.56	3.73	3.97	3.57	3.72	4.11	3.80	3.22	3.58	3.69	0.24
300s	4.07	4.11	4.24	4.48	4.12	4.28	4.62	4.33	3.72	4.12	4.21	0.25
blue 60s	2.37	2.52	2.45	2.53	2.47	2.54	2.45	2.55	2.59	2.51	2.50	0.06
red/blue	1.25	1.04	1.28	1.44	1.09	1.18	1.65	1.25	0.64	1.07	1.19	0.27

log CF and log 300/60 are the logs of the quotients, not the quotients of the logs

Table A.6 PPSL data for SP12334 Milk thistle

A. 7

Irradiated

Aliquot	1	2	3	4	5	6	7	8	9	10	Mean	SD
PSL1A	2239835	2389580	2251653	2251497	2020349	2113526	2340280	2305262	2392432	2349229	2265364.30	120153.90
PSL2A	5183340	11638868	8659582	8582253	6136718	13494784	8906706	5593628	7933861	10465130	8659487.00	2665796.17
CF	2.31	4.87	3.85	3.81	3.04	6.38	3.81	2.43	3.32	4.45	3.83	1.21
PSL1B	2160207	2635798	2123571	2112953	2187821	2063402	2100337	2108261	2153130	2194517	2183999.70	163891.84
PSL2B	21945712	24849015	25022229	18822999	23455960	15865741	26416933	28993047	24002740	21760469	23113484.50	3759105.37
300s	67651741	82385179	83111663	60159608	77391015	51196558	85690020	96765438	77040983	68935234	75032743.90	13315997.02
blue 60s	320983	235265	999504	195166	299050	165143	511614	1059416	730324	279679	479614.40	334595.23
red/blue	68.37	105.62	25.03	96.45	78.43	96.07	51.63	27.37	32.87	77.81	65.97	30.14

Unirradiated

Aliquot	1	2	3	4	5	6	7	8	9	10	Mean	SD
PSL1A	3261	14576	3825	4086	2327	2662	4080	4025	2656	3783	4528.10	3591.61
PSL2A	15130	4695	14685	11933	3035	8935	15706	5090	5474	20061	10474.40	5830.15
CF	4.64	0.32	3.84	2.92	1.30	3.36	3.85	1.26	2.06	5.30	2.89	1.61
PSL1B	2722	3058	3799	2852	3528	3831	2778	3596	3285	3191	3264.00	413.06
PSL2B	6902	4747	1983	2738	1449	6328	4118	10379	4158	4372	4717.40	2630.80
300s	25611	17791	6869	9598	4906	21494	14500	37328	13314	14423	16583.40	9641.53
blue 60s	353	292	388	323	346	378	332	366	361	369	350.80	28.68
red/blue	19.55	16.26	5.11	8.48	4.19	16.74	12.40	28.36	11.52	11.85	13.45	7.19

Log10

Irradiated

Aliquot	1	2	3	4	5	6	7	8	9	10	Mean	SD
PSL1A	6.35	6.38	6.35	6.35	6.31	6.33	6.37	6.36	6.38	6.37	6.35	0.02
PSL2A	6.71	7.07	6.94	6.93	6.79	7.13	6.95	6.75	6.90	7.02	6.92	0.14
CF	0.36	0.69	0.58	0.58	0.48	0.81	0.58	0.38	0.52	0.65	0.56	0.13
PSL1B	6.33	6.42	6.33	6.32	6.34	6.31	6.32	6.32	6.33	6.34	6.34	0.03
PSL2B	7.34	7.40	7.40	7.27	7.37	7.20	7.42	7.46	7.38	7.34	7.36	0.08
300s	7.83	7.92	7.92	7.78	7.89	7.71	7.93	7.99	7.89	7.84	7.87	0.08
blue 60s	5.51	5.37	6.00	5.29	5.48	5.22	5.71	6.03	5.86	5.45	5.59	0.29
red/blue	1.83	2.02	1.40	1.98	1.89	1.98	1.71	1.44	1.52	1.89	1.77	0.24

Unirradiated

Aliquot	1	2	3	4	5	6	7	8	9	10	Mean	SD
PSL1A	3.51	4.16	3.58	3.61	3.37	3.43	3.61	3.60	3.42	3.58	3.59	0.22
PSL2A	4.18	3.67	4.17	4.08	3.48	3.95	4.20	3.71	3.74	4.30	3.95	0.28
CF	0.67	-0.49	0.58	0.47	0.12	0.53	0.59	0.10	0.31	0.72	0.36	0.37
PSL1B	3.43	3.49	3.58	3.46	3.55	3.58	3.44	3.56	3.52	3.50	3.51	0.06
PSL2B	3.84	3.68	3.30	3.44	3.16	3.80	3.61	4.02	3.62	3.64	3.61	0.26
300s	4.41	4.25	3.84	3.98	3.69	4.33	4.16	4.57	4.12	4.16	4.15	0.26
blue 60s	2.55	2.47	2.59	2.51	2.54	2.58	2.52	2.56	2.56	2.57	2.54	0.04
red/blue	1.29	1.21	0.71	0.93	0.62	1.22	1.09	1.45	1.06	1.07	1.07	0.26

log CF and log 300/60 are the logs of the quotients, not the quotients of the logs

Table A.7 PPSL data for SP12335 Dandelion

Irradiated

Aliquot	1	2	3	4	5	6	7	8	9	10	Mean	SD
PSL1A	3261302	3158272	3030178	2961207	3033409	3257423	3224962	2905123	3103457	2779988	3071532.10	160096.12
PSL2A	4020297	3295762	6585897	5011684	4264021	6345622	4049650	4137213	1617510	3923733	4325138.90	1430796.02
CF	1.23	1.04	2.17	1.69	1.41	1.95	1.26	1.42	0.52	1.41	1.41	0.46
PSL1B	3421222	2905678	3460503	2896895	3457561	3121902	2860937	2899932	3211195	2949855	3118568.00	251468.29
PSL2B	7564154	8575757	14125824	11295705	9854096	6392659	7316293	7728237	8846780	7906087	8960559.20	2284500.74
300s	21746921	25639155	43035961	33592198	29778726	18866626	21515562	23297762	27217527	23553613	26824405.10	7144004.02
blue 60s	180725	350737	359913	213992	362355	177719	334570	208263	181272	234269	260381.50	80938.87
red/blue	41.85	24.45	39.25	52.79	27.19	35.97	21.87	37.11	48.80	33.75	34.41	28.23

Unirradiated

Aliquot	1	2	3	4	5	6	7	8	9	10	Mean	SD
PSL1A	2063	6256	2120	2033	2150	2679	2305	2093	2210	3256	2716.50	1299.83
PSL2A	1847	9168	3379	6069	6293	4165	4891	3348	4807	2720	4668.70	2116.92
CF	0.90	1.47	1.59	2.99	2.93	1.55	2.12	1.60	2.18	0.84	1.82	0.74
PSL1B	2072	2549	2166	3609	2289	1718	2391	1958	2203	8609	2956.40	2049.76
PSL2B	1894	1589	2708	2222	2247	699	1434	1941	9802	6014	3055.00	2762.07
300s	6052	5152	8962	6638	8493	2277	4882	6276	33827	21467	10402.60	9724.23
blue 60s	307	312	245	306	277	281	293	250	373	334	297.80	38.19
red/blue	6.17	5.09	11.05	7.26	8.11	2.49	4.89	7.76	26.28	18.01	9.71	7.20

Log10

Irradiated

Aliquot	1	2	3	4	5	6	7	8	9	10	Mean	SD
PSL1A	6.51	6.50	6.48	6.47	6.48	6.51	6.51	6.46	6.49	6.44	6.49	0.02
PSL2A	6.60	6.52	6.82	6.70	6.63	6.80	6.61	6.62	6.21	6.59	6.61	0.17
CF	0.09	0.02	0.34	0.23	0.15	0.29	0.10	0.15	-0.28	0.15	0.12	0.17
PSL1B	6.53	6.46	6.54	6.46	6.54	6.49	6.46	6.46	6.51	6.47	6.49	0.03
PSL2B	6.88	6.93	7.15	7.05	6.99	6.81	6.86	6.89	6.95	6.90	6.94	0.10
300s	7.34	7.41	7.63	7.53	7.47	7.28	7.33	7.37	7.43	7.37	7.42	0.11
blue 60s	5.26	5.54	5.56	5.33	5.56	5.25	5.52	5.32	5.26	5.37	5.40	0.13
red/blue	1.62	1.39	1.59	1.72	1.43	1.56	1.34	1.57	1.69	1.53	1.54	0.12

Unirradiated

Aliquot	1	2	3	4	5	6	7	8	9	10	Mean	SD
PSL1A	3.31	3.80	3.33	3.31	3.33	3.43	3.36	3.32	3.34	3.51	3.40	0.15
PSL2A	3.27	3.96	3.53	3.78	3.80	3.62	3.69	3.52	3.68	3.43	3.63	0.20
CF	-0.05	0.17	0.20	0.47	0.47	0.19	0.33	0.20	0.34	-0.08	0.22	0.19
PSL1B	3.32	3.41	3.34	3.56	3.36	3.24	3.38	3.29	3.34	3.93	3.42	0.20
PSL2B	3.28	3.20	3.43	3.35	3.35	2.84	3.16	3.29	3.99	3.78	3.37	0.32
300s	3.78	3.71	3.95	3.82	3.93	3.36	3.69	3.80	4.53	4.33	3.89	0.33
blue 60s	2.49	2.49	2.39	2.49	2.44	2.45	2.47	2.40	2.57	2.52	2.47	0.06
red/blue	0.79	0.71	1.04	0.86	0.91	0.40	0.69	0.89	1.42	1.26	0.90	0.29

log CF and log 300/60 are the logs of the quotients, not the quotients of the logs

Table A.8 PPSL data for SP12336 Dong quai

A. 9

Irradiated

Aliquot	1	2	3	4	5	6	7	8	9	10	Mean	SD
PSL1A	27243	32105	27913	25625	26616	32608	40132	19422	49343	34815	31582.20	8436.92
PSL2A	272547	171301	60998	215531	232244	363265	206057	127766	228121	108990	198682.00	86702.10
CF	10.00	5.34	2.19	8.41	8.73	11.14	5.13	6.58	4.62	3.13	6.53	2.97
PSL1B	45745	36765	24990	33219	35848	35173	41168	31663	30510	28028	34310.90	6109.11
PSL2B	809113	1225594	474777	1210655	600804	589578	841435	1021442	503027	904701	818112.60	276125.03
300s	2555188	3882452	1495498	3954829	1933324	1881255	2726942	3380908	1621374	2913607	2634537.70	902668.27
blue 60s	6607	19415	23154	16682	2473	4067	12477	29771	11843	13937	14042.60	8577.66
red/blue	122.46	63.13	20.51	72.57	242.95	144.97	67.44	34.31	42.47	64.91	87.57	66.47

Unirradiated

Aliquot	1	2	3	4	5	6	7	8	9	10	Mean	SD
PSL1A	309	270	348	357	416	314	262	345	312	283	321.60	46.45
PSL2A	399	214	460	356	318	315	295	346	369	420	349.20	69.58
CF	1.29	0.79	1.32	1.00	0.76	1.00	1.13	1.00	1.18	1.48	1.10	0.23
PSL1B	328	312	272	389	321	304	376	338	347	290	327.70	36.43
PSL2B	539	388	336	340	506	341	313	244	356	605	396.80	114.33
300s	1266	801	795	627	937	490	465	295	577	1205	745.80	318.61
blue 60s	321	304	255	241	304	326	239	248	284	272	279.40	33.13
red/blue	1.68	1.28	1.32	1.41	1.66	1.05	1.31	0.98	1.25	2.22	1.42	0.36

Log10

Irradiated

Aliquot	1	2	3	4	5	6	7	8	9	10	Mean	SD
PSL1A	4.44	4.51	4.45	4.41	4.43	4.51	4.60	4.29	4.69	4.54	4.49	0.11
PSL2A	5.44	5.23	4.79	5.33	5.37	5.56	5.31	5.11	5.36	5.04	5.25	0.22
CF	1.00	0.73	0.34	0.92	0.94	1.05	0.71	0.82	0.66	0.50	0.77	0.23
PSL1B	4.66	4.57	4.40	4.52	4.55	4.55	4.61	4.50	4.48	4.45	4.53	0.08
PSL2B	5.91	6.09	5.68	6.08	5.78	5.77	5.93	6.01	5.70	5.96	5.89	0.15
300s	6.41	6.59	6.17	6.60	6.29	6.27	6.44	6.53	6.21	6.46	6.40	0.15
blue 60s	3.82	4.29	4.36	4.22	3.39	3.61	4.10	4.47	4.07	4.14	4.05	0.34
red/blue	2.09	1.80	1.31	1.86	2.39	2.16	1.83	1.54	1.63	1.81	1.84	0.31

Unirradiated

Aliquot	1	2	3	4	5	6	7	8	9	10	Mean	SD
PSL1A	2.49	2.43	2.54	2.55	2.62	2.50	2.42	2.54	2.49	2.45	2.50	0.06
PSL2A	2.60	2.33	2.66	2.55	2.50	2.50	2.47	2.54	2.57	2.62	2.53	0.09
CF	0.11	-0.10	0.12	0.00	-0.12	0.00	0.05	0.00	0.07	0.17	0.03	0.09
PSL1B	2.52	2.49	2.43	2.59	2.51	2.48	2.58	2.53	2.54	2.46	2.51	0.05
PSL2B	2.73	2.59	2.53	2.53	2.70	2.53	2.50	2.39	2.55	2.78	2.58	0.12
300s	3.10	2.90	2.90	2.80	2.97	2.69	2.67	2.47	2.76	3.08	2.83	0.20
blue 60s	2.51	2.48	2.41	2.38	2.48	2.51	2.38	2.39	2.45	2.43	2.44	0.05
red/blue	0.23	0.11	0.12	0.15	0.22	0.02	0.12	-0.01	0.10	0.35	0.14	0.10

log CF and log 300/60 are the logs of the quotients, not the quotients of the logs

Table A.9 PPSL data for SP12337 Echinacea

Irradiated

Aliquot	1	2	3	4	5	6	7	8	9	10	Mean	SD
PSL1A	811114	693695	697231	700670	703739	714582	670114	801964	717085	698109	720830.30	46983.56
PSL2A	888838	481917	4726186	1792088	2703268	3121481	2033380	3650091	1589331	2290141	2327672.10	1276711.72
CF	1.10	0.69	6.78	2.56	3.84	4.37	3.03	4.55	2.22	3.28	3.24	1.78
PSL1B	830402	723295	811228	724450	863278	813722	736040	839742	807036	847303	799649.60	52483.19
PSL2B	6321450	8098596	5083877	3621752	5305289	5406490	7359369	6180160	7706997	7506624	6259060.40	1423244.77
300s	19226249	25252851	16137579	11730511	16854215	17350648	23771713	19927646	24785255	24147146	19918381.30	4505192.45
blue 60s	227410	148819	91163	141404	199128	238482	317706	102717	138517	235413	184075.90	71452.06
red/blue	27.80	54.42	55.77	25.61	26.64	22.67	23.16	60.17	55.64	31.89	38.38	15.87

Unirradiated

Aliquot	1	2	3	4	5	6	7	8	9	10	Mean	SD
PSL1A	545	685	545	478	2515	568	1092	568	570	544	811.00	623.46
PSL2A	521	1073	780	972	984	925	730	776	611	3952	1132.40	1005.72
CF	0.96	1.57	1.43	2.03	0.39	1.63	0.67	1.37	1.07	7.26	1.84	1.97
PSL1B	428	463	1122	579	543	612	487	677	587	713	621.10	197.72
PSL2B	2164	1443	2040	1791	2792	2143	7588	1499	2611	1959	2603.00	1802.65
300s	7760	5016	6459	6113	10062	7646	28953	4627	9460	6625	9272.10	7129.90
blue 60s	238	305	325	363	289	273	315	307	308	338	306.10	34.52
red/blue	9.09	4.73	6.28	4.93	9.66	7.85	24.09	4.88	8.48	5.80	8.58	5.75

Log10

Irradiated

Aliquot	1	2	3	4	5	6	7	8	9	10	Mean	SD
PSL1A	5.91	5.84	5.84	5.85	5.85	5.85	5.83	5.90	5.86	5.84	5.86	0.03
PSL2A	5.95	5.68	6.67	6.25	6.43	6.49	6.31	6.56	6.20	6.36	6.29	0.29
CF	0.04	-0.16	0.83	0.41	0.58	0.64	0.48	0.66	0.35	0.52	0.43	0.30
PSL1B	5.92	5.86	5.91	5.86	5.94	5.91	5.87	5.92	5.91	5.93	5.90	0.03
PSL2B	6.80	6.91	6.71	6.56	6.72	6.73	6.87	6.79	6.89	6.88	6.79	0.11
300s	7.28	7.40	7.21	7.07	7.23	7.24	7.38	7.30	7.39	7.38	7.29	0.11
blue 60s	5.36	5.17	4.96	5.15	5.30	5.38	5.50	5.01	5.14	5.37	5.23	0.17
red/blue	1.44	1.74	1.75	1.41	1.43	1.36	1.36	1.78	1.75	1.50	1.55	0.18

Unirradiated

Aliquot	1	2	3	4	5	6	7	8	9	10	Mean	SD
PSL1A	2.74	2.84	2.74	2.68	3.40	2.75	3.04	2.75	2.76	2.74	2.84	0.22
PSL2A	2.72	3.03	2.89	2.99	2.99	2.97	2.86	2.89	2.79	3.60	2.97	0.24
CF	-0.02	0.19	0.16	0.31	-0.41	0.21	-0.17	0.14	0.03	0.86	0.13	0.33
PSL1B	2.63	2.67	3.05	2.76	2.73	2.79	2.69	2.83	2.77	2.85	2.78	0.12
PSL2B	3.34	3.16	3.31	3.25	3.45	3.33	3.88	3.18	3.42	3.29	3.36	0.20
300s	3.89	3.70	3.81	3.79	4.00	3.88	4.46	3.67	3.98	3.82	3.90	0.22
blue 60s	2.38	2.48	2.51	2.56	2.46	2.44	2.50	2.49	2.49	2.53	2.48	0.05
red/blue	0.96	0.67	0.80	0.69	0.99	0.89	1.38	0.69	0.93	0.76	0.88	0.21

log CF and log 300/60 are the logs of the quotients, not the quotients of the logs

Table A.10 PPSL data for SP12338 *Gingko biloba*

Irradiated		PSL1A	PSL2A	CF	PSL1B	PSL2B	CF
Siberian ginseng	Mean	488.40	1038.40	2.18	506.00	4580.20	9.24
	SD	136.14	461.21	0.96	143.99	3012.66	6.07
	Log Mean	2.68	2.98	0.30	2.69	3.55	0.86
	Log SD	0.10	0.19	0.19	0.12	0.35	0.34
Alfalfa	Mean	2160861.10	6386829.80	2.92	2073918.20	17512788.00	8.56
	SD	111405.88	2637505.63	1.12	198106.53	5155608.50	2.77
	Log Mean	6.33	6.77	0.43	6.31	7.22	0.90
	Log SD	0.02	0.20	0.18	0.04	0.18	0.19
Green tea	Mean	43930.10	230460.00	5.78	40690.20	511892.70	13.34
	SD	12001.92	146089.19	4.53	8220.23	224156.84	7.48
	Log Mean	4.63	5.26	0.63	4.60	5.67	1.07
	Log SD	0.13	0.35	0.37	0.09	0.19	0.23
Saw palmetto	Mean	1649.70	2849.40	1.50	1980.00	14315.20	8.45
	SD	466.77	3751.38	1.48	723.26	6835.65	6.05
	Log Mean	3.20	3.20	0.00	3.27	4.11	0.84
	Log SD	0.11	0.46	0.40	0.16	0.23	0.29
Guarana	Mean	19035.10	20391.10	1.10	13035.30	53522.00	4.27
	SD	9569.82	17773.42	0.64	3523.71	37258.85	3.07
	Log Mean	4.24	4.19	-0.05	4.10	4.67	0.57
	Log SD	0.19	0.33	0.32	0.12	0.21	0.22
Milk thistle	Mean	127297.60	42649.50	0.33	129033.80	190655.30	1.46
	SD	18614.35	20122.82	0.13	19469.17	64103.09	0.37
	Log Mean	5.10	4.59	-0.51	5.11	5.25	0.15
	Log SD	0.06	0.18	0.15	0.06	0.17	0.13
Dandelion	Mean	2265364.30	8659487.00	3.83	2183999.70	23113484.50	10.61
	SD	120153.90	2665796.17	1.21	163891.84	3759105.37	1.79
	Log Mean	6.35	6.92	0.56	6.34	7.36	1.02
	Log SD	0.02	0.14	0.13	0.03	0.08	0.07
Dong quai	Mean	3071532.10	4325138.90	1.41	3118568.00	8960559.20	2.87
	SD	160096.12	1430796.02	0.46	251468.29	2284500.74	0.65
	Log Mean	6.49	6.61	0.12	6.49	6.94	0.45
	Log SD	0.02	0.17	0.17	0.03	0.10	0.09
Echinacea	Mean	31582.20	198682.00	6.53	34310.90	818112.60	24.15
	SD	8436.92	86702.10	2.97	6109.11	276125.03	8.28
	Log Mean	4.49	5.25	0.77	4.53	5.89	1.36
	Log SD	0.11	0.22	0.23	0.08	0.15	0.15
Gingko biloba	Mean	720830.30	2327672.10	3.24	799649.60	6259060.40	7.86
	SD	46983.56	1276711.72	1.78	52483.19	1423244.77	1.97
	Log Mean	5.86	6.29	0.43	5.90	6.79	0.88
	Log SD	0.03	0.29	0.30	0.03	0.11	0.11

Table A11 Mean terminal counts and concentration factors for irradiated products (PSL1A and B are initial readings, PSL2A and B are readings after separation; method A is settling, method B includes density separation). Highlights indicate promotion from negative to intermediate (yellow) and intermediate to positive (green) as a result of concentration.

Unirradiated		PSL1A	PSL2A	CF	PSL1B	PSL2B	CF
Siberian ginseng	Mean	280.00	287.90	1.04	314.50	285.50	0.95
	SD	36.06	39.82	0.20	67.34	61.10	0.30
	Mean	2.44	2.46	0.01	2.49	2.45	-0.04
	SD	0.06	0.06	0.08	0.09	0.09	0.13
Alfalfa	Mean	1963.80	3906.40	1.99	1729.50	14667.50	8.46
	SD	295.63	1489.00	0.70	145.97	2946.17	1.40
	Log Mean	3.29	3.56	0.28	3.24	4.16	0.92
	Log SD	0.06	0.16	0.15	0.04	0.09	0.08
Green tea	Mean	501.10	340.70	0.69	463.60	593.10	1.30
	SD	68.35	37.92	0.11	49.39	293.89	0.70
	Log Mean	2.70	2.53	-0.17	2.66	2.73	0.07
	Log SD	0.05	0.05	0.07	0.04	0.19	0.21
Saw palmetto	Mean	325.90	317.10	1.03	270.70	341.10	1.27
	SD	82.14	81.84	0.38	35.12	68.47	0.25
	Log Mean	2.50	2.49	-0.01	2.43	2.53	0.10
	Log SD	0.10	0.11	0.15	0.05	0.08	0.09
Guarana	Mean	492.20	431.10	0.90	513.00	2555.20	5.27
	SD	112.16	226.88	0.47	148.03	1130.36	2.66
	Log Mean	2.68	2.59	-0.09	2.70	3.38	0.68
	Log SD	0.10	0.18	0.19	0.11	0.16	0.19
Milk thistle	Mean	3119.70	635.50	0.23	4031.20	5619.50	1.57
	SD	873.92	355.74	0.15	2642.38	3252.34	0.89
	Log Mean	3.48	2.75	-0.73	3.55	3.69	0.14
	Log SD	0.13	0.22	0.29	0.22	0.24	0.23
Dandelion	Mean	4528.10	10474.40	2.89	3264.00	4717.40	1.46
	SD	3591.61	5830.15	1.61	413.06	2630.80	0.78
	Log Mean	3.59	3.95	0.36	3.51	3.61	0.10
	Log SD	0.22	0.28	0.37	0.06	0.26	0.27
Dong quai	Mean	2716.50	4668.70	1.82	2956.40	3055.00	1.15
	SD	1299.83	2116.92	0.74	2049.76	2762.07	1.18
	Log Mean	3.40	3.63	0.22	3.42	3.37	-0.05
	Log SD	0.15	0.20	0.19	0.20	0.32	0.28
Echinacea	Mean	321.60	349.20	1.10	327.70	396.80	1.24
	SD	46.45	69.58	0.23	36.43	114.33	0.42
	Log Mean	2.50	2.53	0.03	2.51	2.58	0.07
	Log SD	0.06	0.09	0.09	0.05	0.12	0.14
Gingko biloba	Mean	811.00	1132.40	1.84	621.10	2603.00	4.67
	SD	623.46	1005.72	1.97	197.72	1802.65	3.99
	Log Mean	2.84	2.97	0.13	2.78	3.36	0.58
	Log SD	0.22	0.24	0.33	0.12	0.20	0.26

Table A12 Mean terminal counts and concentration factors for unirradiated products (PSL1A and B are initial readings, PSL2A and B are readings after separation; method A is settling, method B includes density separation). Highlights indicate promotion from negative to intermediate (yellow) and intermediate to positive (green) as a result of concentration.

A. 14

Appendix B Data for stimulation with multiple wavelengths

	Siberian ginseng		Alfalfa		Green tea		Saw palmetto		Guarana	
	red	blue	red	blue	red	blue	red	blue	red	blue
Irr 1	3043	347	19458412	378406	276846	3154	12497	311	56465	770
2	7151	1884	23072315	524599	617066	2118	21734	571	154575	1790
3	3959	313	14479870	25929	464584	33285	18043	1134	32635	903
4	2123	322	5814317	424392	423625	14926	24305	276	31637	1375
5	8683	395	15165584	256595	998324	27704	22075	826	62512	6657
6	2463	775	21836832	148776	585793	5371	14002	3551	29577	1079
7	6868	684	16170726	216912	660267	45040	8413	392	34895	593
8	8822	386	16290063	288324	527368	11449	6452	358	49764	1204
9	707	365	20949546	118506	338788	21891	5941	362	36199	421
10	1983	296	21890215	133188	226266	17805	9690	291	46961	801
Mean	4580.20	576.70	17512788.00	251562.70	511892.70	18274.30	14315.20	807.20	53522.00	1559.30
SD	3012.66	487.63	5155608.50	155018.90	224156.84	13975.71	6835.65	1003.25	37258.85	1834.51
Unirr 1	404	288	16348	278	703	287	300	259	2153	313
2	224	309	9094	450	295	244	241	269	2540	459
3	312	292	13232	343	711	249	304	283	2521	299
4	197	240	12587	343	606	337	491	256	1916	409
5	267	301	19338	356	468	276	317	339	2318	314
6	332	308	13467	404	287	285	303	306	5436	303
7	255	309	15304	363	504	268	378	289	3285	343
8	245	259	13701	328	498	310	338	305	1594	289
9	287	279	18240	513	536	258	398	291	2243	268
10	332	298	15364	340	1323	276	341	309	1546	281
Mean	285.50	288.30	14667.50	371.80	593.10	279.00	341.10	290.60	2555.20	327.80
SD	61.10	23.07	2946.17	67.33	293.89	28.15	68.47	25.49	1130.36	60.70

Table B.1a Red and Blue pulsed PSL for SP10950-4

	Milk thistle		Dandelion		Dong quai		Echinacea		*Gingko biloba*	
	red	blue	red	blue	red	blue	red	blue	red	blue
Irr 1	244107	2741	21945712	320983	7564154	180725	809113	6607	6321450	227410
2	226246	565	24849015	235265	8575757	350737	1225594	19415	8098596	148819
3	268045	939	25022229	999504	14125824	359913	474777	23154	5083877	91163
4	246739	2211	18822999	195166	11295705	213992	1210655	16682	3621752	141404
5	233264	479	23455960	299050	9854096	362355	600804	2473	5305289	199128
6	91287	934	15865741	165143	6392659	177719	589578	4067	5406490	238482
7	126318	528	26416933	511614	7316293	334570	841435	12477	7359369	317706
8	105846	339	28993047	1059416	7728237	208263	1021442	29771	6180160	102717
9	165541	981	24002740	730324	8846780	181272	503027	11843	7706997	138517
10	199160	2104	21760469	279679	7906087	234269	904701	13937	7506624	235413
Mean	190655.30	1182.10	23113484.50	479614.40	8960559.20	260381.50	818112.60	14042.60	6259060.40	184075.90
SD	64103.09	850.73	3759105.37	334595.23	2284500.74	80938.87	276125.03	8577.66	1423244.77	71452.06
Unirr 1	4160	232	6902	353	1894	307	539	321	2164	238
2	3637	332	4747	292	1589	312	388	304	1443	305
3	5386	284	1983	388	2708	245	336	255	2040	325
4	9412	339	2738	323	2222	306	340	241	1791	363
5	3706	298	1449	346	2247	277	506	304	2792	289
6	5279	346	6328	378	699	281	341	326	2143	273
7	12794	285	4118	332	1434	293	313	239	7588	315
8	6348	357	10379	366	1941	250	244	248	1499	307
9	1665	385	4158	361	9802	373	356	284	2611	308
10	3808	325	4372	369	6014	334	605	272	1959	338
Mean	5619.50	318.30	4717.40	350.80	3055.00	297.80	396.80	279.40	2603.00	306.10
SD	3252.34	44.12	2630.80	28.68	2762.07	38.19	114.33	33.13	1802.65	34.52

Table B.1b Red and Blue pulsed PSL for SP12334-8

B. 3

Appendix C Process flow chart for PSL pre-concentration

```
                    ┌─────────────────┐
                    │   M g sample    │
                    └─────────────────┘
                             │
                             ▼
                    ┌─────────────────┐
                    │  in V1 ml liquid │
                    │  in V2 ml beaker │
                    └─────────────────┘
                             │
                             ▼
                    ┌─────────────────┐
                    │ 5 min ultrasonic│
                    └─────────────────┘
                             │
                             ▼
                        ◇ is sieving
                          necessary? ◇
                    yes  /        \  no
                       ▼            ▼
          ┌─────────────────┐   ┌──────────────────────┐
          │      sieve      │   │   centrifuge then    │
          │  through150µm   │   │  density separation  │
          │      sieve      │   └──────────────────────┘
          └─────────────────┘
                 │
                 ▼
          ┌─────────────────┐
          │    allow to     │
          │   settle 30     │
          │      min        │
          └─────────────────┘
                      │
                      ▼
              ┌──────────────────┐
              │  decant liquid   │
              │  then settle 2   │
              │ min in 100 ml    │
              │      water       │
              └──────────────────┘
                      │
                      ▼
              ┌──────────────────┐
              │  decant water    │
              │ transfer sample  │
              │   to planchet    │
              └──────────────────┘
                      │
                      ▼
              ┌──────────────────┐
              │       PSL        │
              └──────────────────┘
```
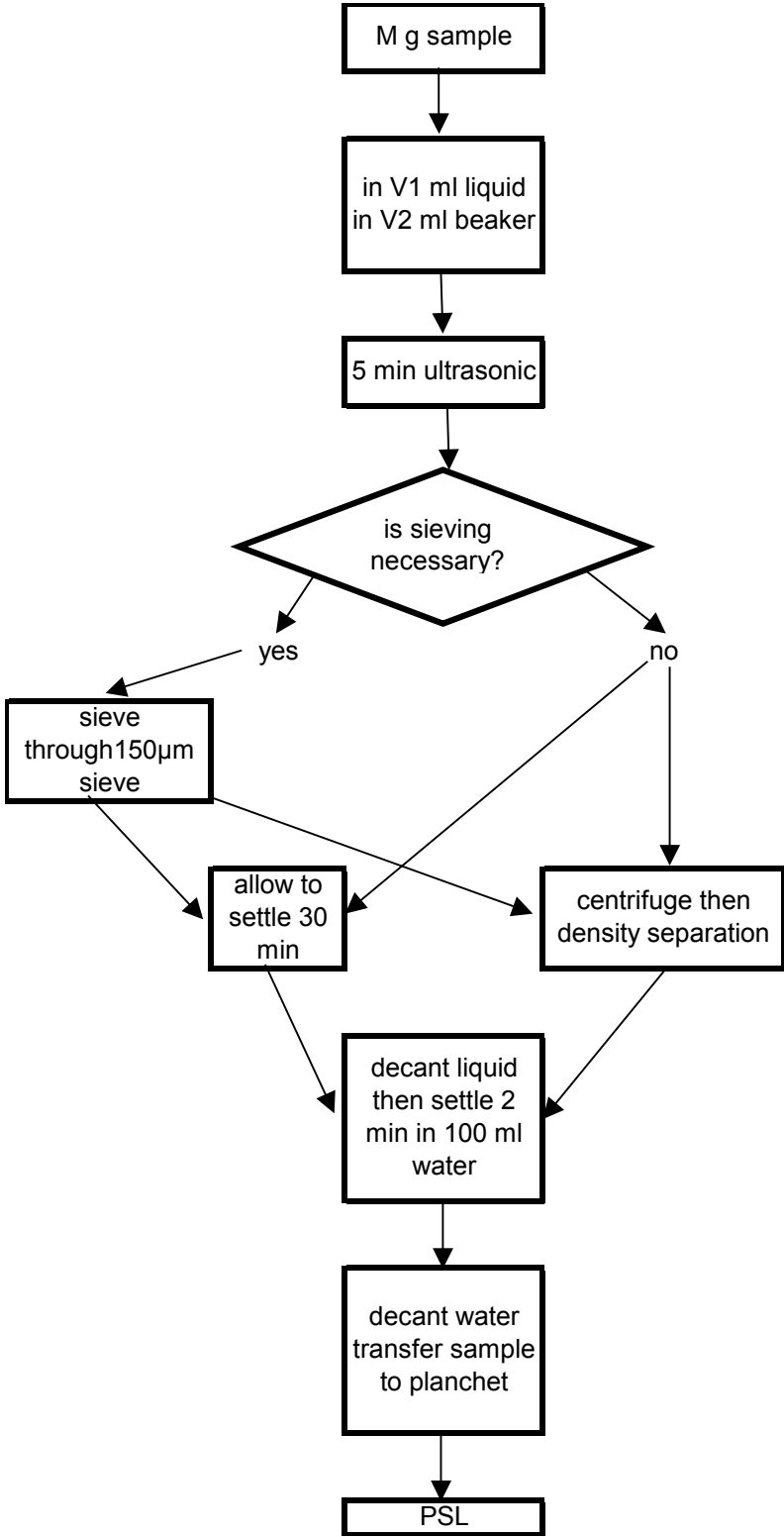
Chart C.1 Suggested decision tree for signal enhancement using either settling in a liquid or density separation

C. 2

Appendix D Simulated calibrated PSL, depletion rate and dual wavelength stimulation plots
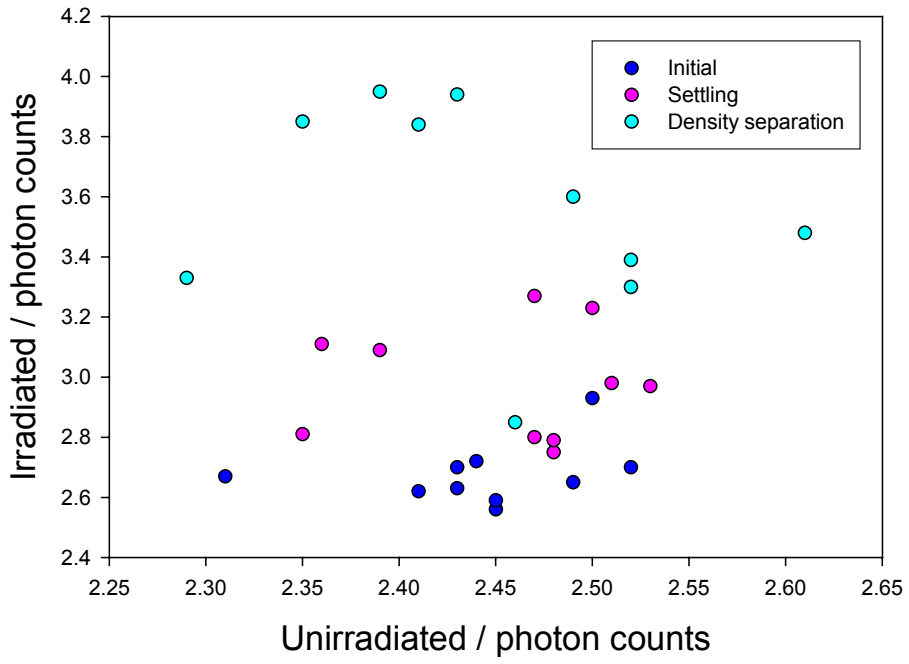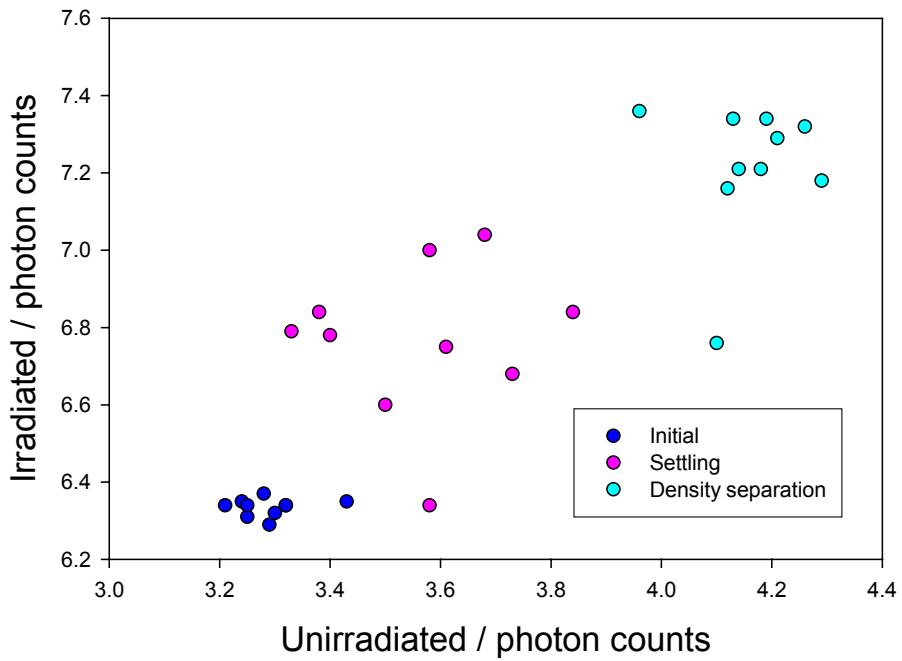
Figure D.1 "Calibrated" plots for Siberian ginseng and Alfalfa
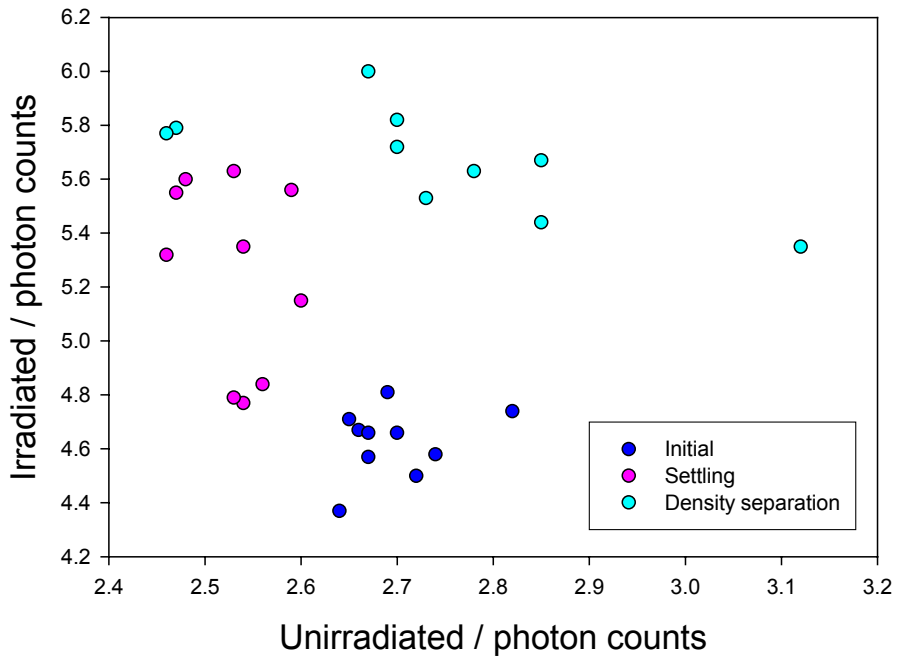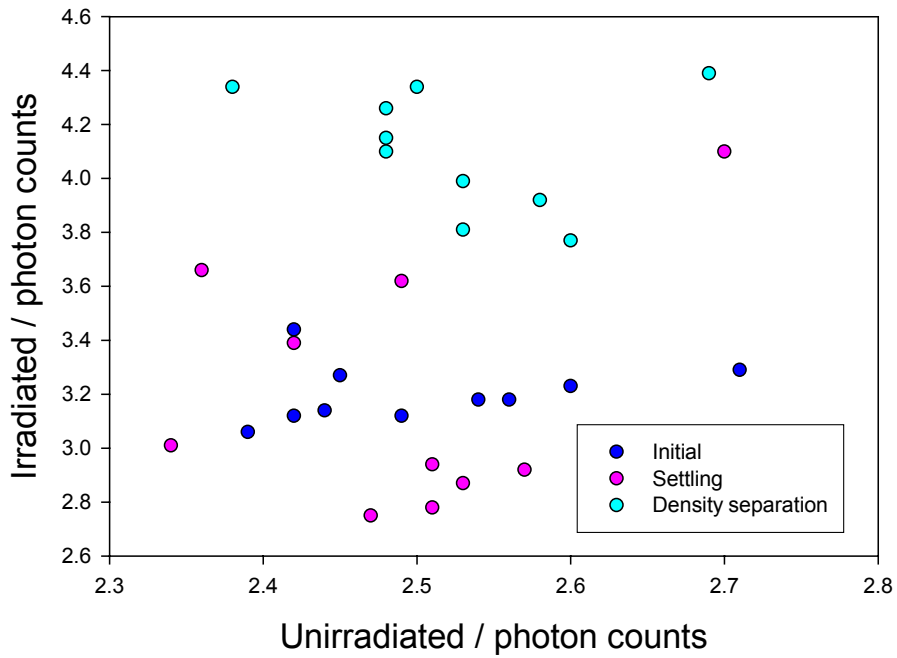
Figure D.2 "Calibrated" plots for Green tea and Saw palmetto

Guarana
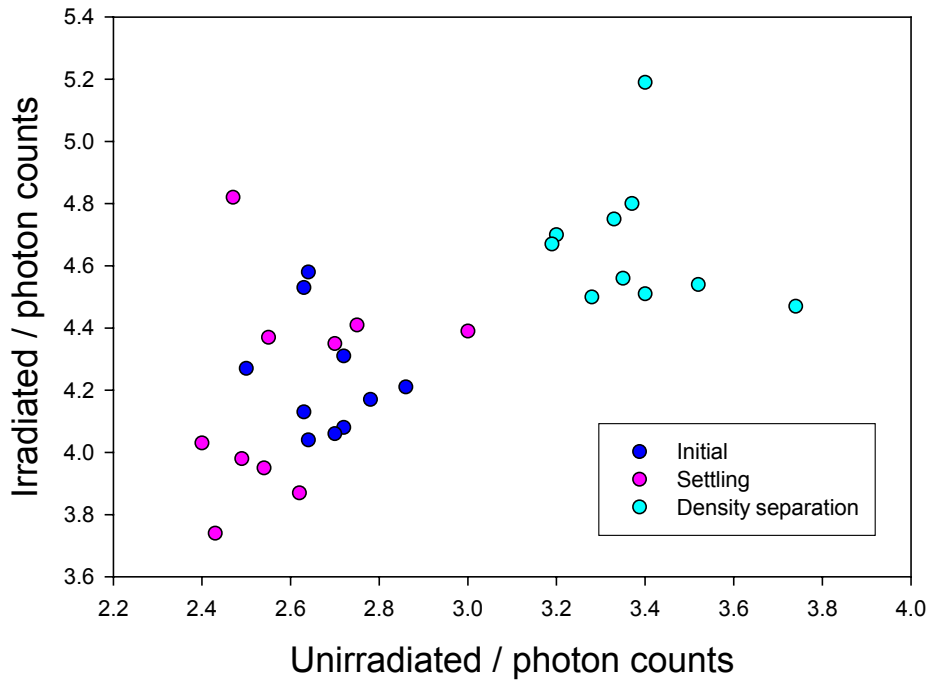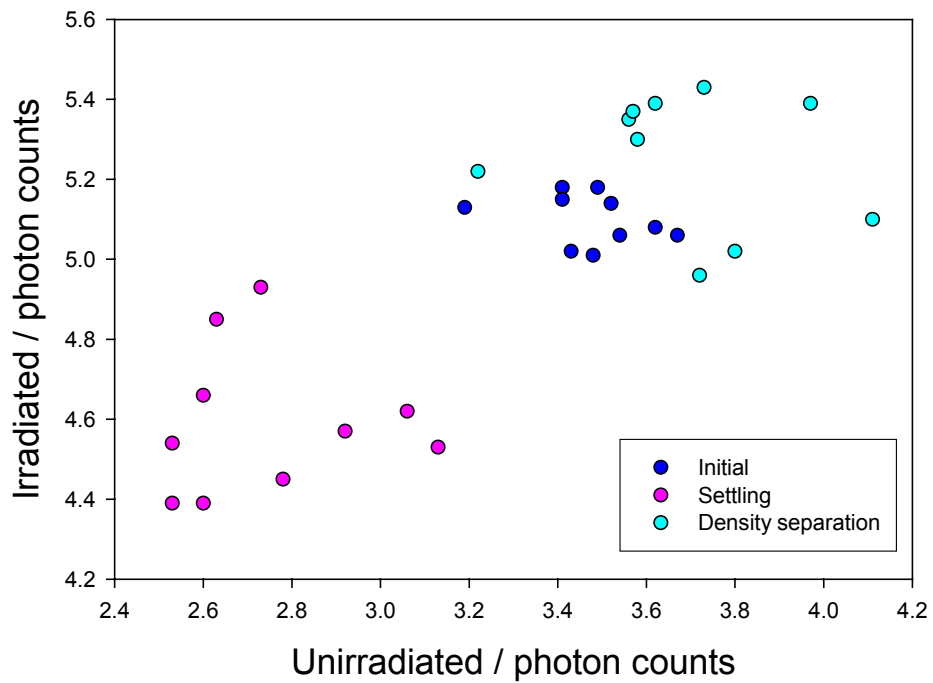
Milk thistle

Figure D.3 "Calibrated" plots for Guarana and Milk thistle

Dandelion
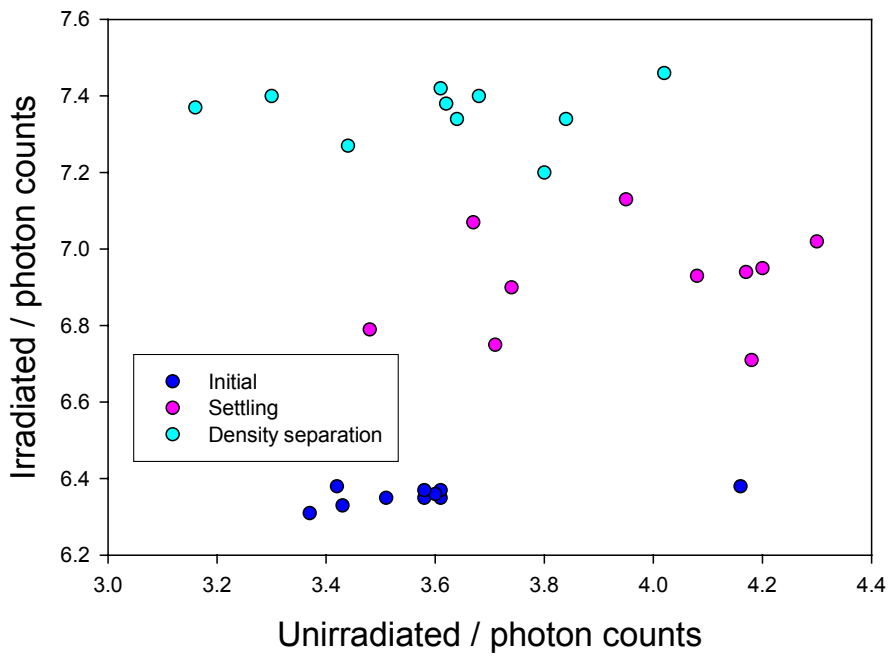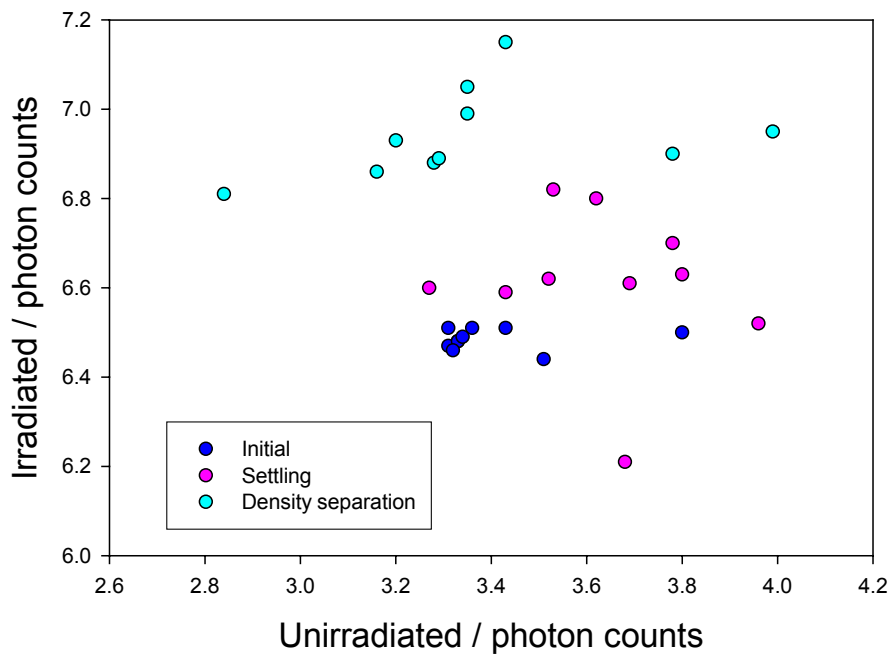
Dong quai

Figure D.4 "Calibrated" plots for Dandelion and Dong quai
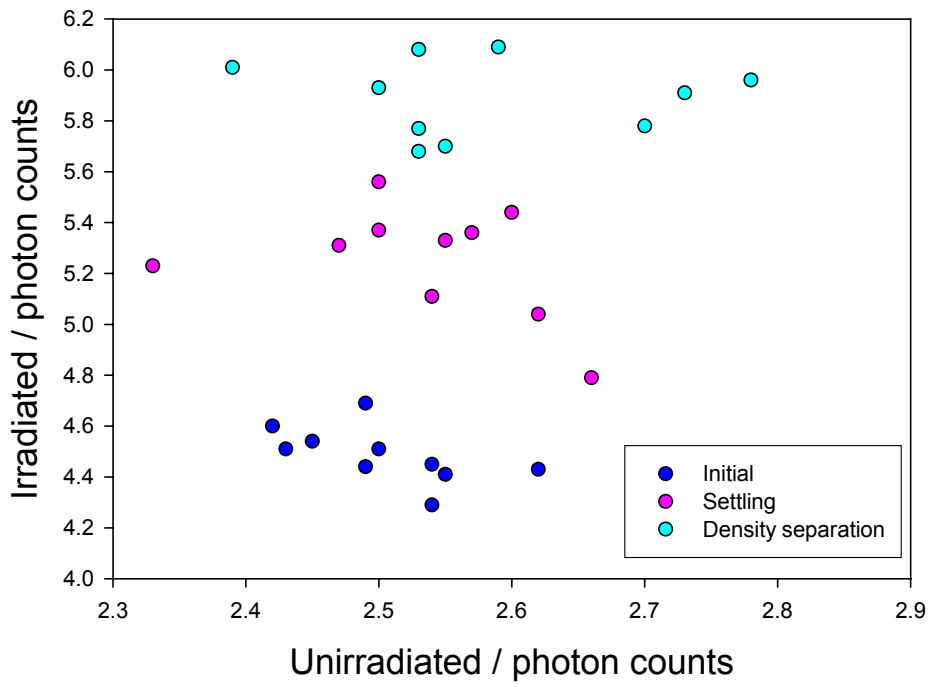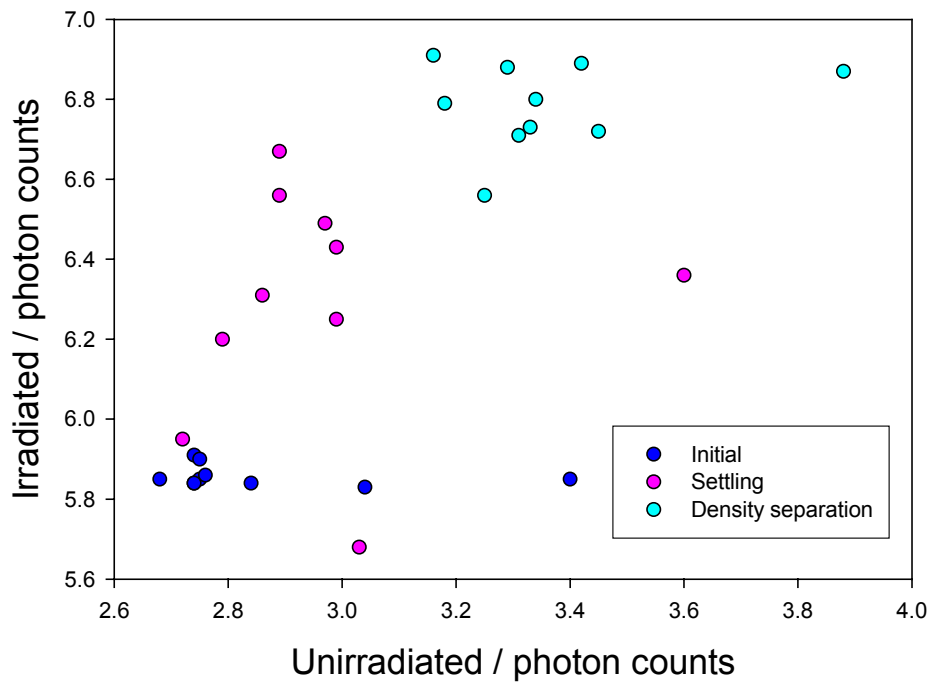
Figure D.5 "Calibrated" plots for Echinacea and *Gingko biloba*
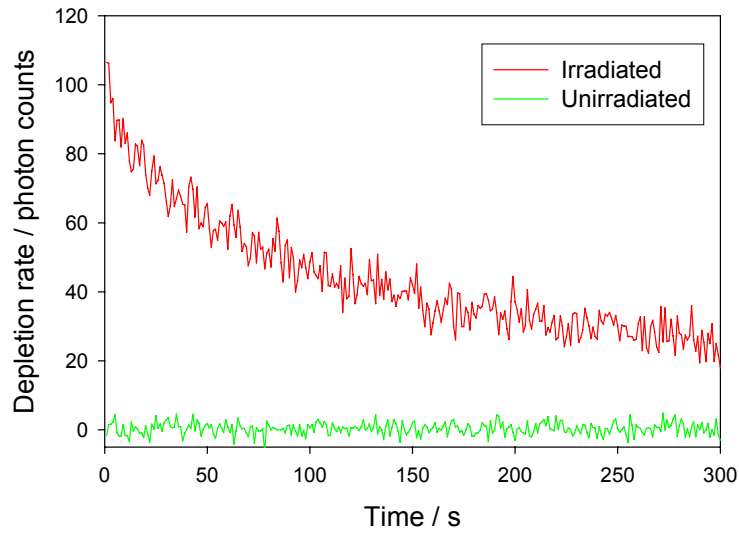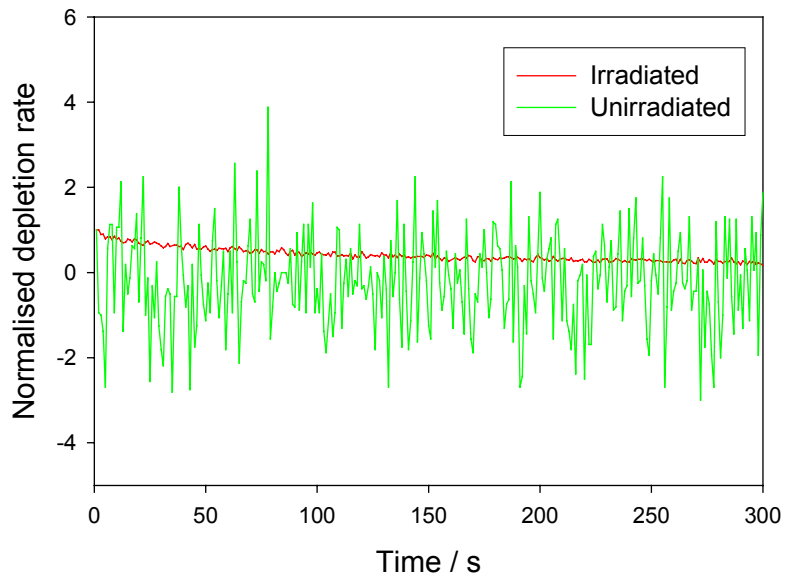
Figure D.6 Mean and normalized depletion rate curves for SP10950 Siberian ginseng

Mean depletion rate
Alfalfa
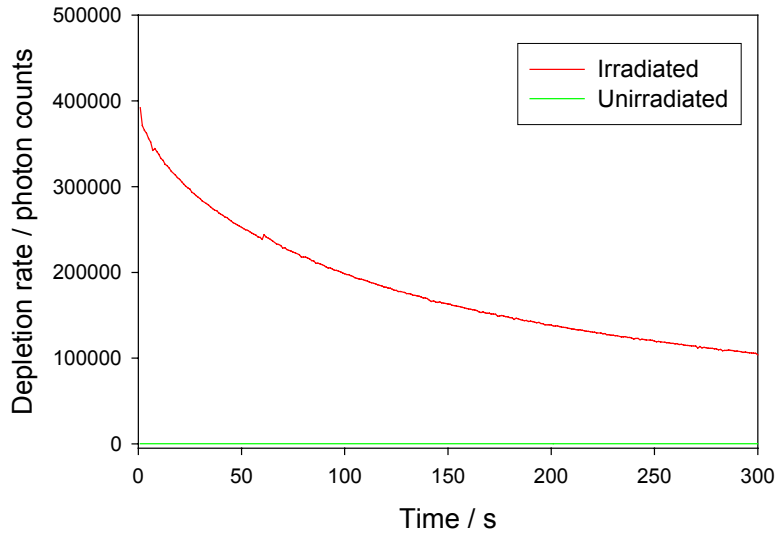
Normalised mean depletion rate
Alfalfa
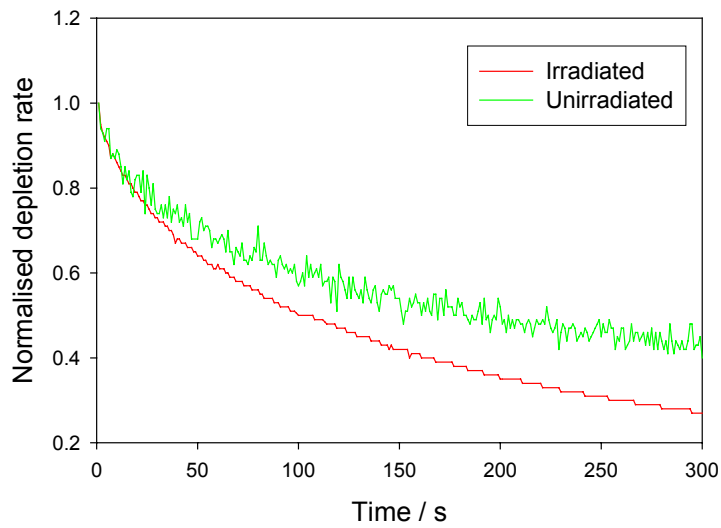
Figure D.7 Mean and normalized depletion rate curves for SP10951 Alfalfa
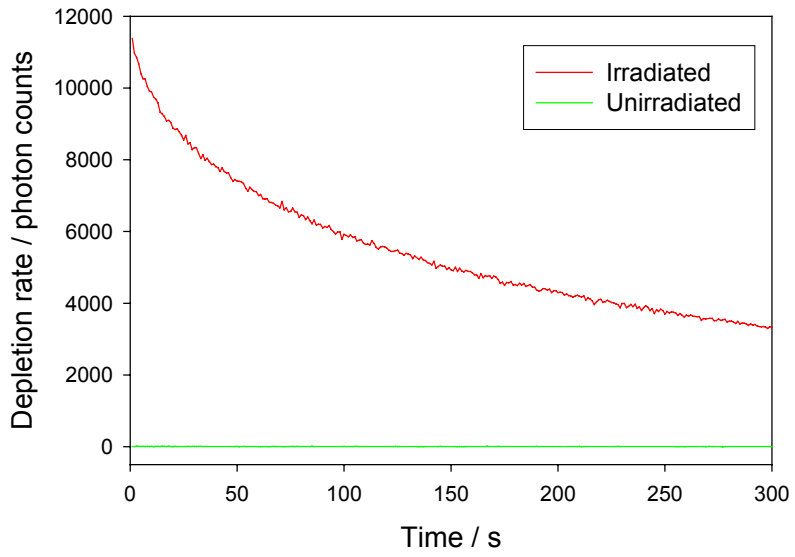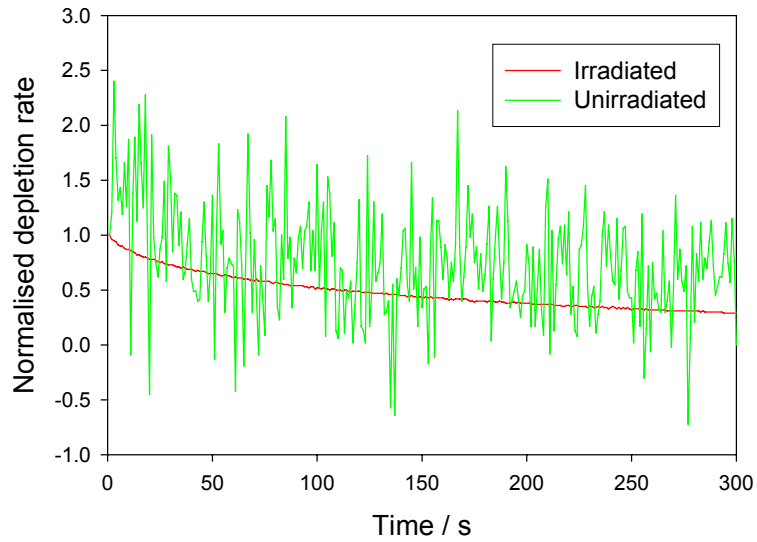
Figure D.8 Mean and normalized depletion rate curves for SP10952 Green tea

Mean depletion rate
Saw palmetto
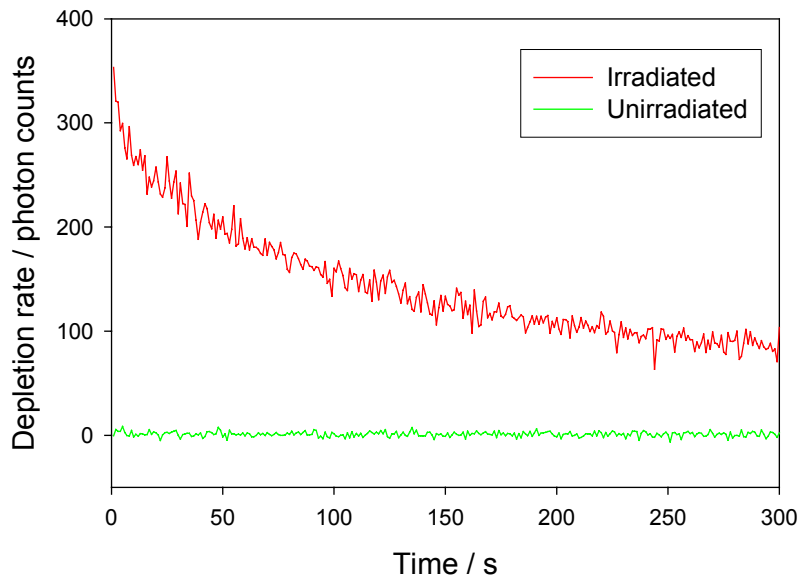
Normalised mean depletion rate
Saw palmetto
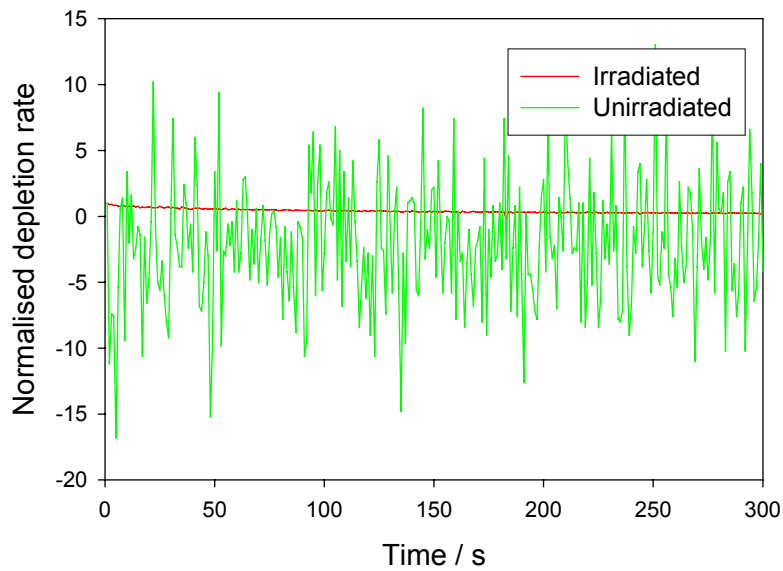
Figure D.9 Mean and normalized depletion rate curves for SP10953 Saw palmetto
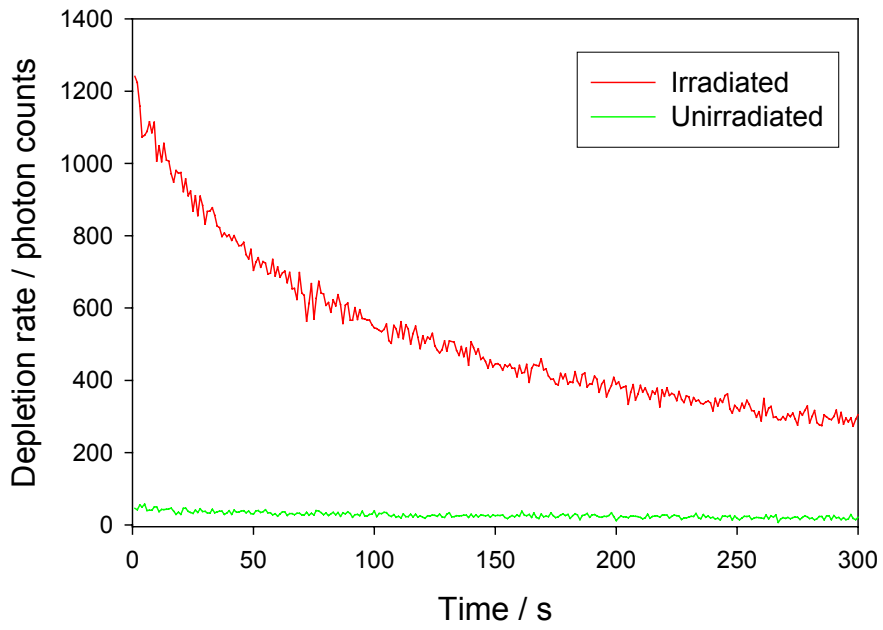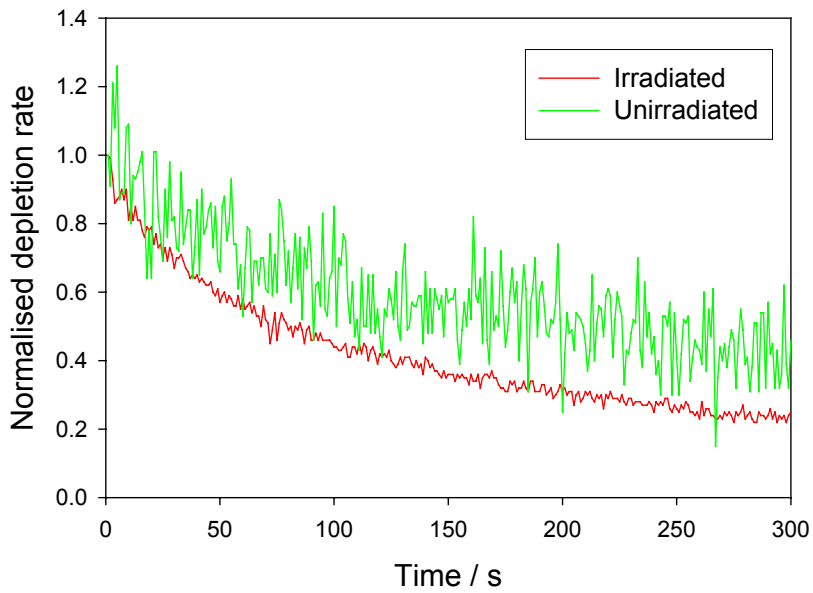
Figure D.10 Mean and normalized depletion rate curves for SP10954 Guarana
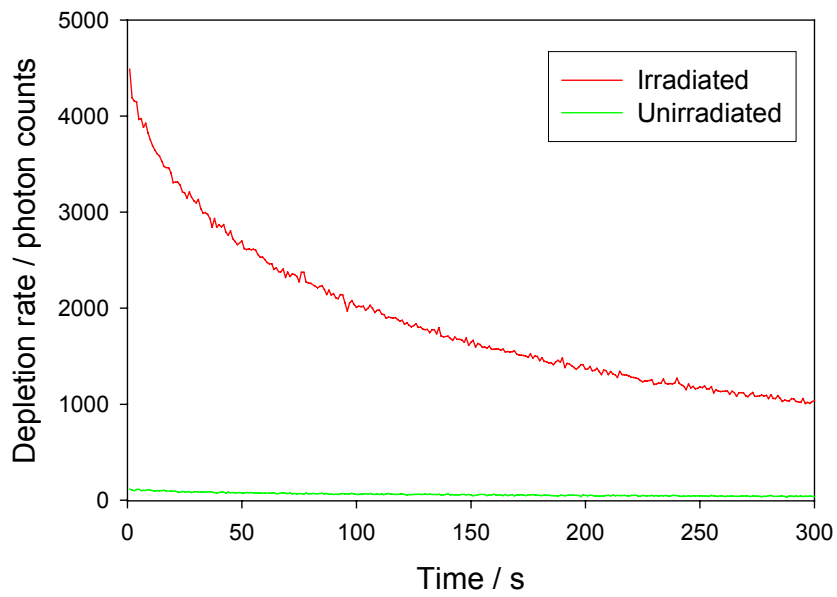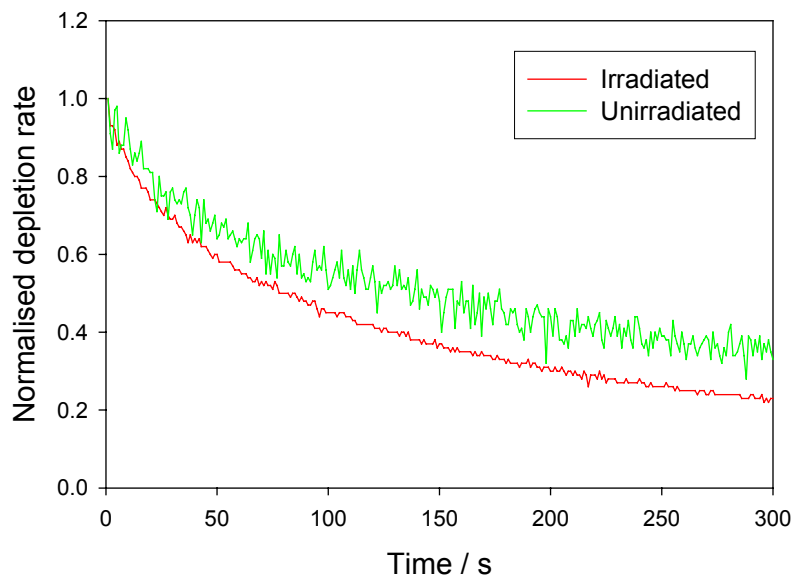
Figure D.11 Mean and normalized depletion rate curves for SP12334 Milk thistle
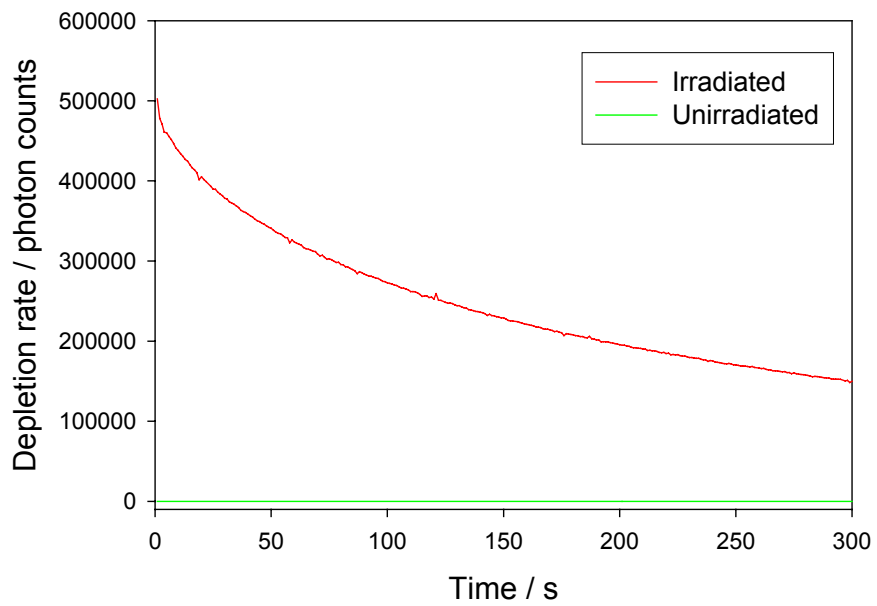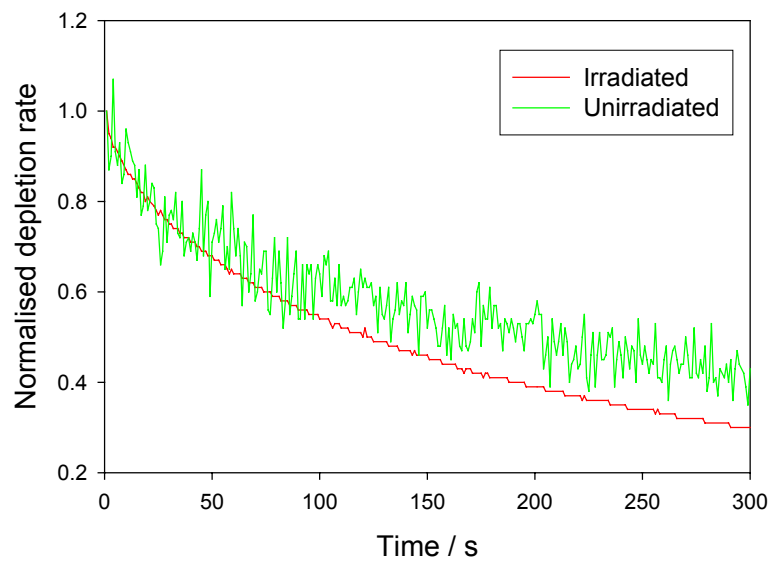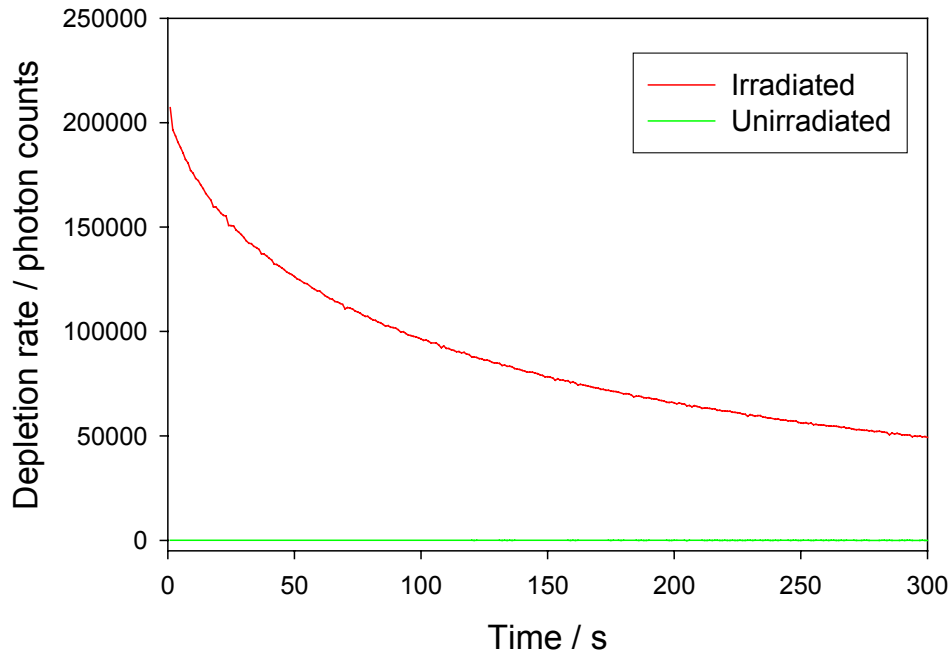
Figure D.12 Mean and normalized depletion rate curves for SP12335 Dandelion

Mean depletion rate
Dong quai

Normalised mean depletion rate
Dong quai
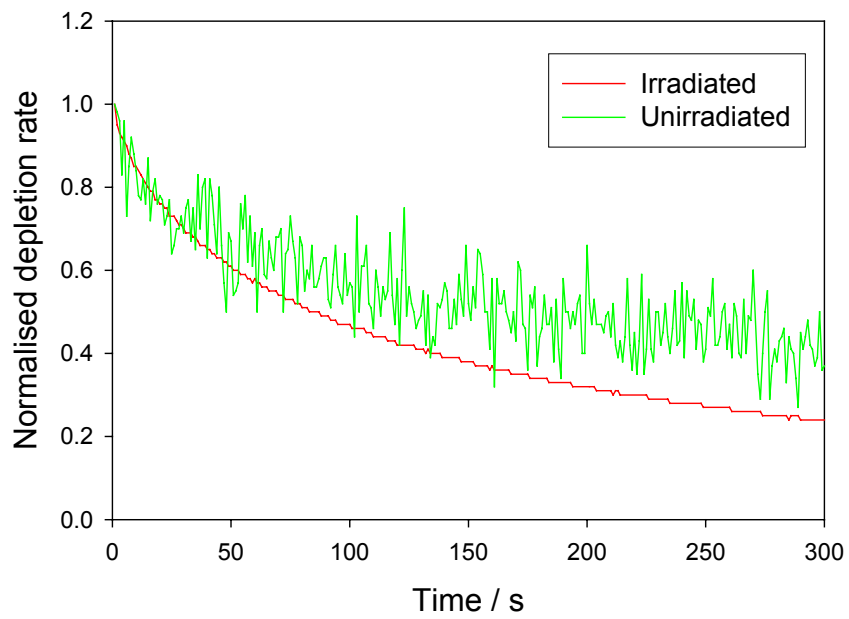
Figure D.13 Mean and normalized depletion rate curves for SP12336 Dong quai
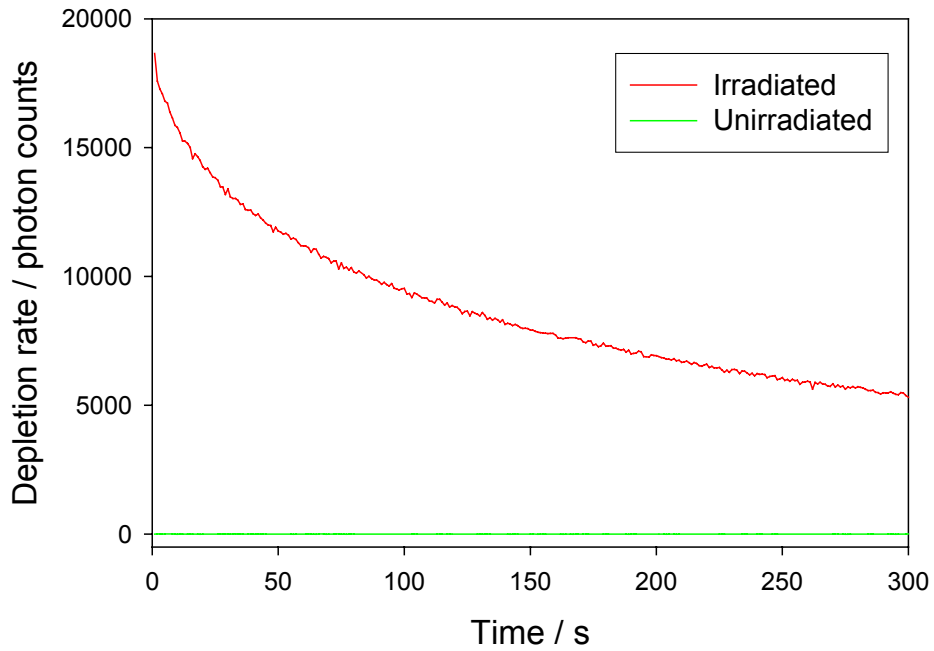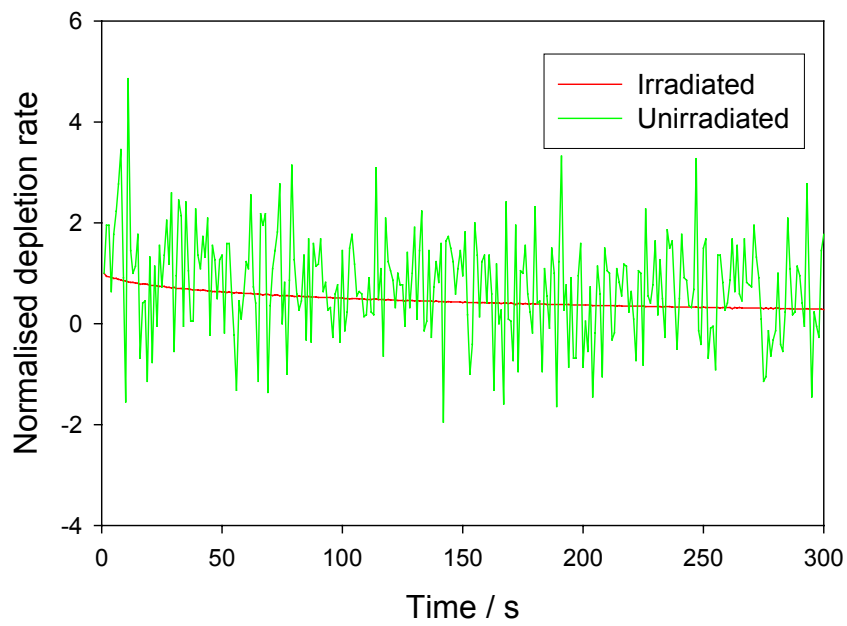
Figure D.14 Mean and normalized depletion rate curves for SP12337 Echinacea

Mean depletion rate
Gingko biloba
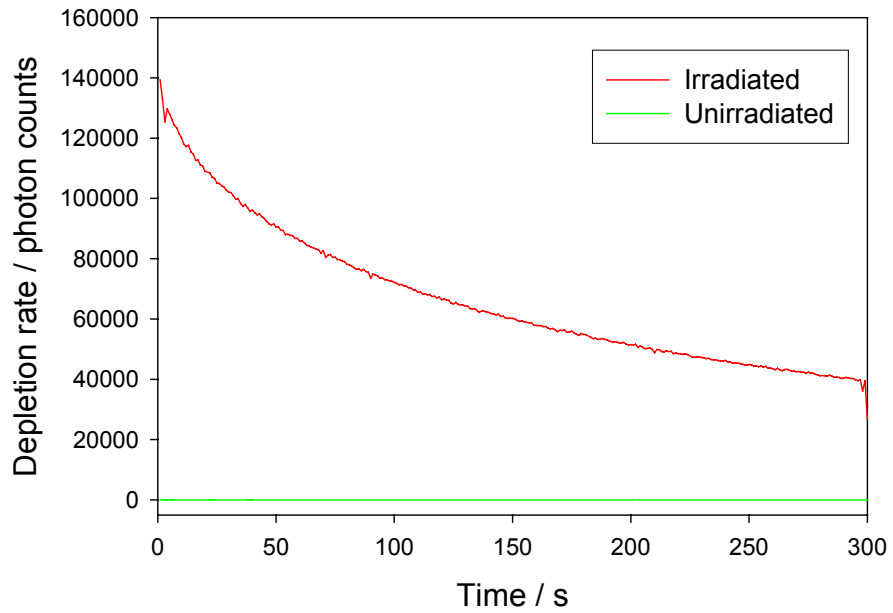
Normalised mean depletion rate
Gingko biloba
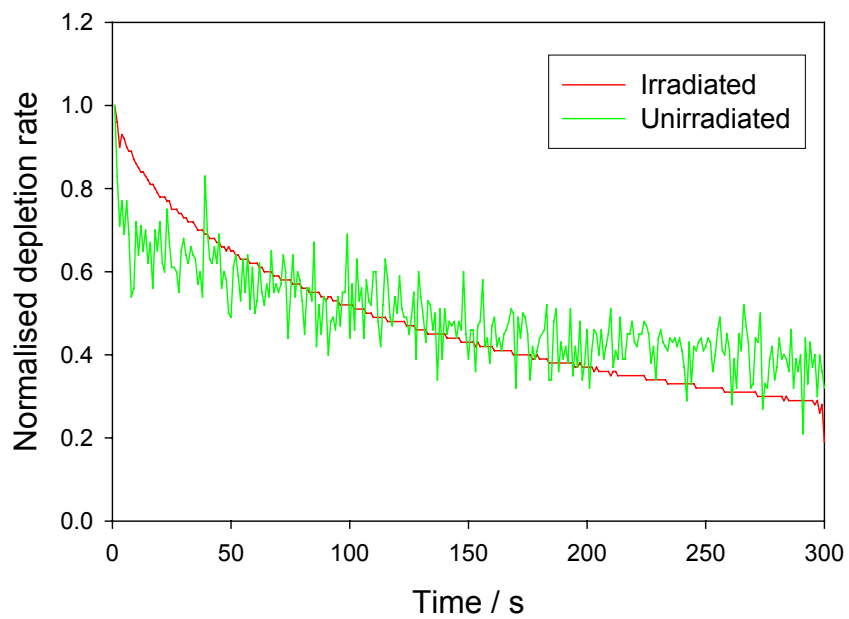
Figure D.15 Mean and normalized depletion rate curves for SP12338 *Gingko biloba*
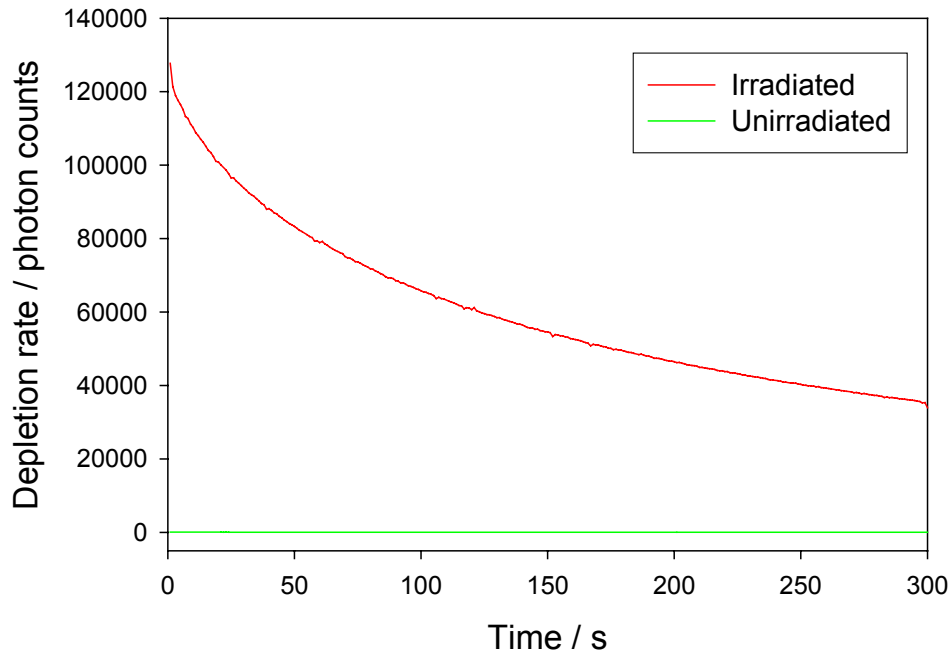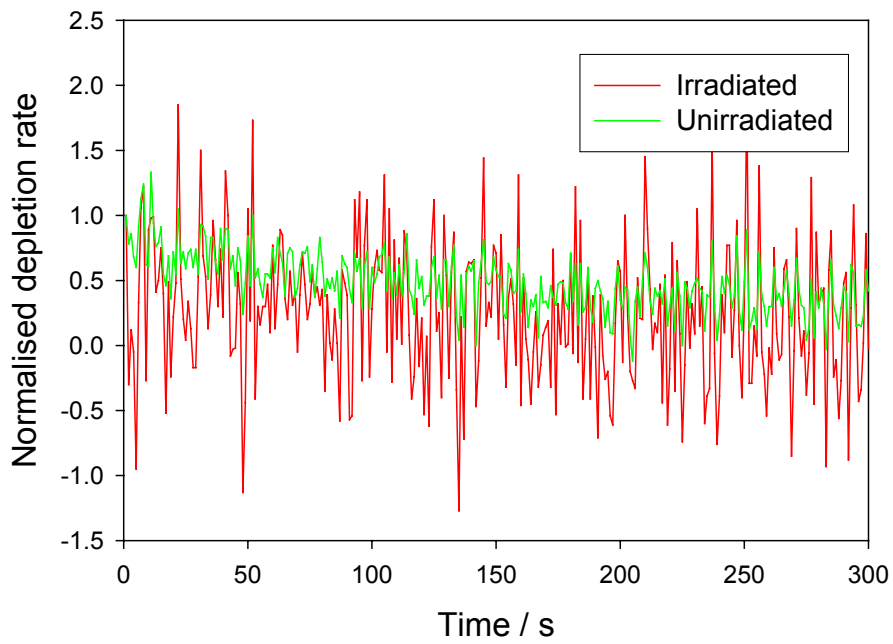
Figure D.16 Mean and normalized global depletion rate curves for all ten samples
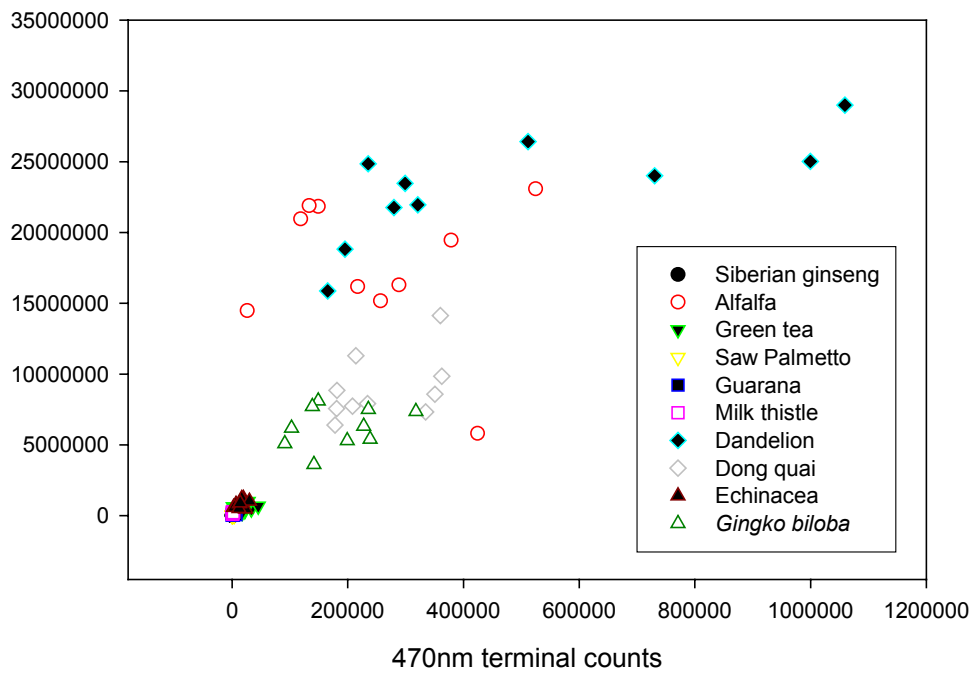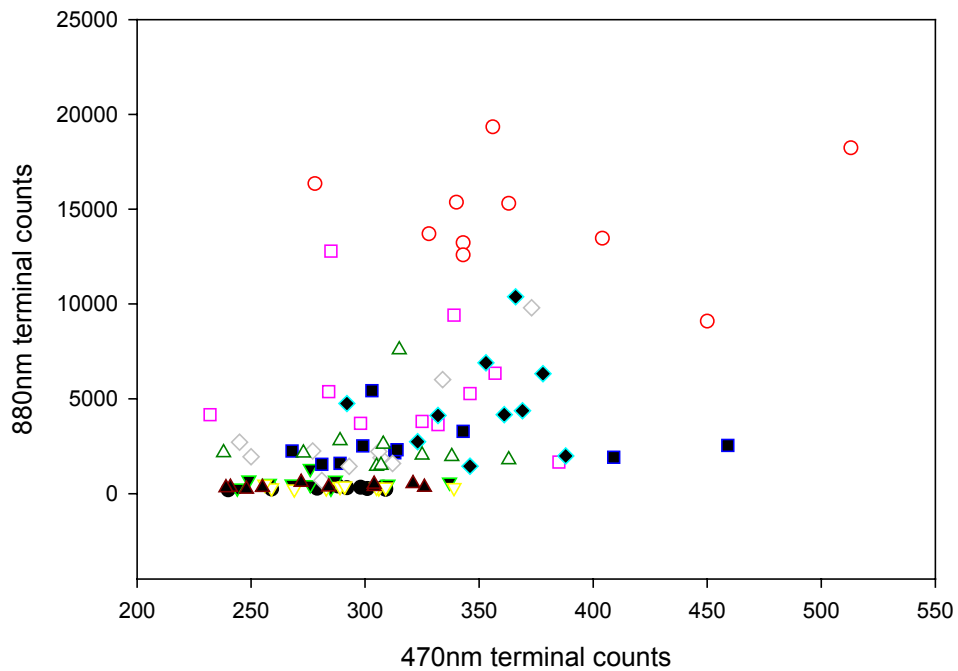
Figure D.17 Red vs blue 60 second measurements (10-fold replication)

Figure D.18 Expanded plot for lower sensitivity irradiated samples: red vs blue 60 second measurements (10-fold replication)

Appendix E : Red/blue statistics from 2-fold replication of all sample

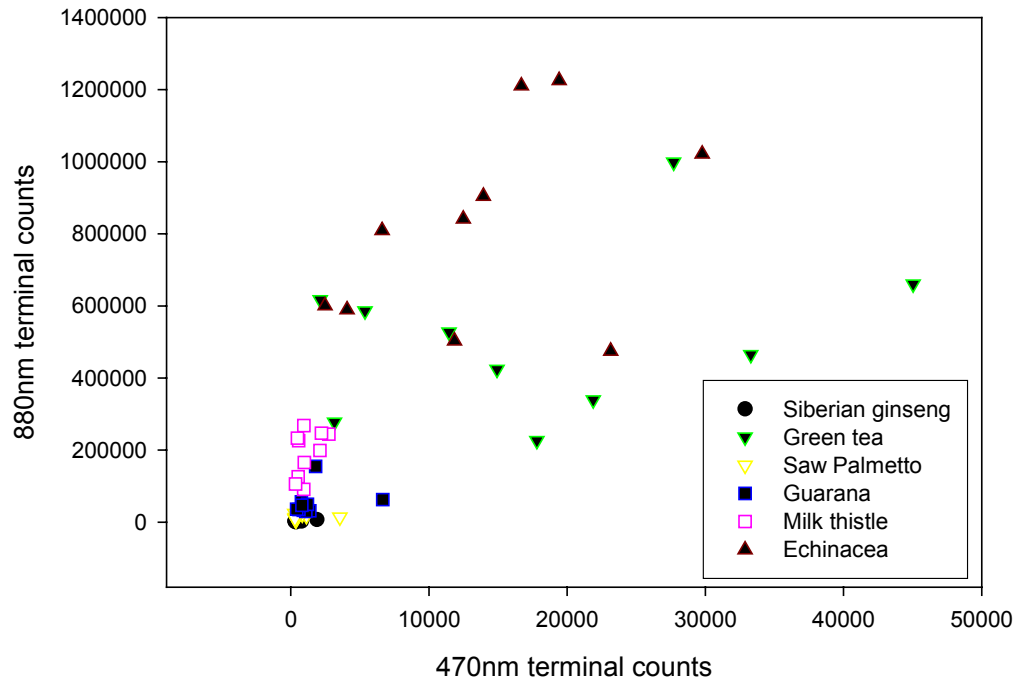| Irradiated	Siberian ginseng		Alfalfa		Green tea		Saw palmetto		Guarana	
IRSL										
B1	42.00	79.00	43.00	84.00	64.00	79.00	69.00	58.00	39.00	32.00
Error	6.48	8.89	6.56	9.17	8.00	8.89	8.31	7.62	6.24	5.66
B2	79.00	63.00	125.00	69.00	52.00	107.00	45.00	85.00	58.00	103.00
Error	8.89	7.94	11.18	8.31	7.21	10.34	6.71	9.22	7.62	10.15
Bkgd /cps	6.05	7.10	8.40	7.65	5.80	9.30	5.70	7.15	4.85	6.75
Error	0.55	0.60	0.65	0.62	0.54	0.68	0.53	0.60	0.49	0.58
Total signal	417.00	576.00	45509.00	3988.00	523.00	593.00	551.00	806.00	1342.00	3151.00
Error	20.42	24.00	213.33	63.15	22.87	24.35	23.47	28.39	36.63	56.13
Net signal	-127.50	-63.00	44753.00	3299.50	1.00	-244.00	38.00	162.50	905.50	2543.50
Error	53.55	58.75	221.16	84.18	53.59	66.03	53.47	60.84	57.50	76.71
Depletion index	0.81	0.97	1.63	1.50	0.89	1.13	0.96	1.12	1.16	1.39
Error	0.18	0.20	0.11	0.19	0.19	0.23	0.20	0.21	0.19	0.19
OSL										
B1	79.00	63.00	125.00	69.00	52.00	107.00	45.00	85.00	58.00	103.00
Error	8.89	7.94	11.18	8.31	7.21	10.34	6.71	9.22	7.62	10.15
B2	142.00	83.00	195.00	130.00	60.00	86.00	83.00	89.00	97.00	117.00
Error	11.92	9.11	13.96	11.40	7.75	9.27	9.11	9.43	9.85	10.82
Bkgd /cps	11.05	7.30	16.00	9.95	5.60	9.65	6.40	8.70	7.75	11.00
Error	0.74	0.60	0.89	0.71	0.53	0.69	0.57	0.66	0.62	0.74
Total signal	1167.00	1069.00	90041.00	8630.00	3345.00	4077.00	1908.00	2539.00	2754.00	8526.00
Error	34.16	32.70	300.07	92.90	57.84	63.85	43.68	50.39	52.48	92.34
Net signal	172.50	412.00	88601.00	7734.50	2841.00	3208.50	1332.00	1756.00	2056.50	7536.00
Error	75.11	63.45	310.68	112.52	74.92	89.36	67.08	77.86	76.76	113.93
Depletion index	1.12	1.06	1.87	1.36	1.00	1.12	1.20	1.19	1.19	1.45
Error	0.19	0.18	0.11	0.14	0.13	0.14	0.18	0.17	0.16	0.15
IRSL/OSL	-0.74	-0.15	0.51	0.43	0.00	-0.08	0.03	0.09	0.44	0.34
Error	-0.45	-0.14	0.00	0.01	0.02	-0.02	0.04	0.03	0.03	0.01

Table E.1 : Red/blue statistics from 2-fold replication of all samples

Irradiated	Milk thistle		Dandelion		Dong quai		Echinacea		Gingko biloba	
IRSL										
B1	57.00	65.00	73.00	69.00	80.00	58.00	51.00	75.00	80.00	77.00
Error	7.55	8.06	8.54	8.31	8.94	7.62	7.14	8.66	8.94	8.77
B2	58.00	76.00	141.00	67.00	123.00	112.00	56.00	45.00	90.00	99.00
Error	7.62	8.72	11.87	8.19	11.09	10.58	7.48	6.71	9.49	9.95
Bkgd /cps	5.75	7.05	10.70	6.80	10.15	8.50	5.35	6.00	8.50	8.80
Error	0.54	0.59	0.73	0.58	0.71	0.65	0.52	0.55	0.65	0.66
Total signal	678.00	1082.00	63147.00	25570.00	97238.00	55101.00	1001.00	511.00	74838.00	13076.00
Error	26.04	32.89	251.29	159.91	311.83	234.74	31.64	22.61	273.57	114.35
Net signal	160.50	447.50	62184.00	24958.00	96324.50	54336.00	519.50	-29.00	74073.00	12284.00
Error	54.83	62.75	259.77	168.30	318.35	241.96	56.28	54.23	279.79	129.00
Depletion index	1.09	1.11	1.54	1.46	1.57	1.60	1.44	1.52	1.54	1.51
Error	0.21	0.19	0.10	0.12	0.09	0.10	0.26	0.32	0.09	0.14
OSL										
B1	58.00	76.00	141.00	67.00	123.00	112.00	56.00	45.00	90.00	99.00
Error	7.62	8.72	11.87	8.19	11.09	10.58	7.48	6.71	9.49	9.95
B2	84.00	68.00	210.00	113.00	308.00	204.00	110.00	70.00	315.00	106.00
Error	9.17	8.25	14.49	10.63	17.55	14.28	10.49	8.37	17.75	10.30
Bkgd /cps	7.10	7.20	17.55	9.00	21.55	15.80	8.30	5.75	20.25	10.25
Error	0.60	0.60	0.94	0.67	1.04	0.89	0.64	0.54	1.01	0.72
Total signal	1606.00	1888.00	114342.00	44707.00	183405.00	112468.00	4452.00	2759.00	164563.00	32185.00
Error	40.07	43.45	338.14	211.44	428.26	335.36	66.72	52.53	405.66	179.40
Net signal	967.00	1240.00	112762.50	43897.00	181465.50	111046.00	3705.00	2241.50	162740.50	31262.50
Error	66.94	69.31	348.50	219.89	438.33	344.77	88.39	71.33	415.65	190.62
Depletion index	1.14	1.30	1.62	1.48	1.70	1.93	1.30	1.13	1.58	1.42
Error	0.18	0.20	0.09	0.10	0.08	0.11	0.16	0.16	0.08	0.11
IRSL/OSL	0.17	0.36	0.55	0.57	0.53	0.49	0.14	-0.01	0.46	0.39
Error	0.06	0.05	0.00	0.00	0.00	0.00	0.02	-0.02	0.00	0.00

Table E.2 : Red/blue statistics from 2-fold replication of all samples

Unirradiated	Siberian ginseng		Alfalfa		Green tea		Saw palmetto		Guarana	
IRSL										
B1	68.00	89.00	45.00	86.00	66.00	52.00	51.00	64.00	82.00	78.00
Error	8.25	9.43	6.71	9.27	8.12	7.21	7.14	8.00	9.06	8.83
B2	87.00	87.00	83.00	57.00	32.00	51.00	77.00	55.00	51.00	78.00
Error	9.33	9.33	9.11	7.55	5.66	7.14	8.77	7.42	7.14	8.83
Bkgd /cps	7.75	8.80	6.40	7.15	4.90	5.15	6.40	5.95	6.65	7.80
Error	0.62	0.66	0.57	0.60	0.49	0.51	0.57	0.55	0.58	0.62
Total signal	569.00	706.00	469.00	605.00	435.00	488.00	551.00	660.00	770.00	670.00
Error	23.85	26.57	21.66	24.60	20.86	22.09	23.47	25.69	27.75	25.88
Net signal	-128.50	-86.00	-107.00	-38.50	-6.00	24.50	-25.00	124.50	171.50	-32.00
Error	60.89	65.35	55.33	59.17	49.19	50.73	56.06	55.41	58.85	61.88
Depletion index	1.14	0.78	0.91	0.97	0.90	0.91	0.97	1.06	1.06	1.14
Error	0.23	0.15	0.19	0.20	0.20	0.19	0.20	0.21	0.20	0.22
OSL										
B1	87.00	87.00	83.00	57.00	32.00	51.00	77.00	55.00	51.00	78.00
Error	9.33	9.33	9.11	7.55	5.66	7.14	8.77	7.42	7.14	8.83
B2	133.00	70.00	62.00	84.00	52.00	67.00	71.00	78.00	99.00	90.00
Error	11.53	8.37	7.87	9.17	7.21	8.19	8.43	8.83	9.95	9.49
Bkgd /cps	11.00	7.85	7.25	7.05	4.20	5.90	7.40	6.65	7.50	8.40
Error	0.74	0.63	0.60	0.59	0.46	0.54	0.61	0.58	0.61	0.65
Total signal	1195.00	1231.00	2502.00	3431.00	2952.00	3020.00	1347.00	1565.00	1237.00	1496.00
Error	34.57	35.09	50.02	58.57	54.33	54.95	36.70	39.56	35.17	38.68
Net signal	205.00	524.50	1849.50	2796.50	2574.00	2489.00	681.00	966.50	562.00	740.00
Error	75.17	66.41	73.74	79.29	68.21	73.55	65.91	65.26	65.38	69.99
Depletion index	0.99	0.88	1.08	1.00	0.97	0.99	0.94	1.06	0.95	1.12
Error	0.17	0.15	0.15	0.13	0.13	0.13	0.15	0.17	0.16	0.18
IRSL/OSL	-0.63	-0.16	-0.06	-0.01	0.00	0.01	-0.04	0.13	0.31	-0.04
Error	-0.38	-0.13	-0.03	-0.02	-0.02	0.02	-0.08	0.06	0.11	-0.08

Table E.3 : Red/blue statistics from 2-fold replication of all samples

Unirradiated	Milk thistle		Dandelion		Dong quai		Echinacea		Gingko biloba	
IRSL										
B1	62.00	47.00	35.00	44.00	46.00	65.00	56.00	96.00	50.00	77.00
Error	7.87	6.86	5.92	6.63	6.78	8.06	7.48	9.80	7.07	8.77
B2	86.00	73.00	55.00	74.00	53.00	94.00	46.00	90.00	65.00	106.00
Error	9.27	8.54	7.42	8.60	7.28	9.70	6.78	9.49	8.06	10.30
Bkgd /cps	7.40	6.00	4.50	5.90	4.95	7.95	5.10	9.30	5.75	9.15
Error	0.61	0.55	0.47	0.54	0.50	0.63	0.50	0.68	0.54	0.68
Total signal	452.00	493.00	466.00	486.00	400.00	487.00	388.00	610.00	632.00	706.00
Error	21.26	22.20	21.59	22.05	20.00	22.07	19.70	24.70	25.14	26.57
Net signal	-214.00	-47.00	61.00	-45.00	-45.50	-228.50	-71.00	-227.00	114.50	-117.50
Error	58.73	54.06	47.84	53.62	49.04	60.88	49.53	66.16	54.41	66.42
Depletion index	0.98	1.11	1.28	1.23	1.37	1.13	1.19	1.01	1.40	1.00
Error	0.21	0.23	0.28	0.26	0.31	0.24	0.27	0.20	0.28	0.19
OSL										
B1	86.00	73.00	55.00	74.00	53.00	94.00	46.00	90.00	65.00	106.00
Error	9.27	8.54	7.42	8.60	7.28	9.70	6.78	9.49	8.06	10.30
B2	117.00	69.00	66.00	66.00	48.00	39.00	105.00	144.00	99.00	98.00
Error	10.82	8.31	8.12	8.12	6.93	6.24	10.25	12.00	9.95	9.90
Bkgd /cps	10.15	7.10	6.05	7.00	5.05	6.65	7.55	11.70	8.20	10.20
Error	0.71	0.60	0.55	0.59	0.50	0.58	0.61	0.76	0.64	0.71
Total signal	1144.00	1135.00	1975.00	2319.00	1263.00	1163.00	1537.00	3306.00	4180.00	2677.00
Error	33.82	33.69	44.44	48.16	35.54	34.10	39.20	57.50	64.65	51.74
Net signal	230.50	496.00	1430.50	1689.00	808.50	564.50	857.50	2253.00	3442.00	1759.00
Error	72.49	63.33	66.52	71.79	57.52	62.10	67.78	89.69	86.61	82.51
Depletion index	1.00	0.94	1.03	1.07	0.88	1.09	0.98	1.01	1.00	1.05
Error	0.17	0.16	0.16	0.15	0.15	0.19	0.16	0.13	0.12	0.15
IRSL/OSL	-0.93	-0.09	0.04	-0.03	-0.06	-0.40	-0.08	-0.10	0.03	-0.07
Error	-0.39	-0.11	0.03	-0.03	-0.06	-0.12	-0.06	-0.03	0.02	-0.04

Table E.4 : Red/blue statistics from 2-fold replication of all samples