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

CONTRACT NUMBER A05010

TASK 1 : REVIEW OF EXISTING DATA SETS

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SUMMARY

This report forms the first deliverable of project A05010 aimed at optimising the photostimulated luminescence screening method for dietary supplements. The work follows a series of surveys of undeclared irradiated foods conducted since 2001 which have shown substantial evidence of irradiated ingredients and products within the dietary supplement field. Over the same period producers and retailers have also conducted significant studies of raw materials in support of regulatory compliance. The dietary supplements themselves are a very diverse product set. Whereas the EN13751 photostimulated luminescence (PSL) method, and EN1788 thermoluminescence (TL) were originally developed and validated for herbs, spices, seafoods and fruits and vegetables, their application to dietary supplements has resulted in extension of the fields of application; in some cases to poorly defined sample matrices whose luminescence sensitivities are not well established. While the TL method involves explicit separation of silicate phases followed by sensitivity-calibrated TL analysis, PSL screening in its simplest form searches for radiation induced luminescence from essentially unprepared samples. While EN13751 recommends the use of the calibrated PSL protocol for materials of unknown sensitivity, this has not always been followed in studies of dietary supplements, and may in any case be of limited use in complex mixtures of diverse ingredients.

In this study it is intended to explore the possibilities of developing pre-concentration techniques to improve PSL performance with products whose sensitivities are limited by low mineral concentrations. Also, once mineral concentrates are available, to explore the potential of using depletion–rate analysis and multi-wavelength stimulation to enhance the method. In the initial stage a review has been conducted of available data sets where PSL data had been collected together with TL data from dietary supplements and their ingredients. The correspondence between both methods has been examined and combinations identified where different types of mixed outcomes were encountered. From 10 official survey sets a subset of 280 samples was examined for which PSL screening and TL analysis were available. Within these a subset of 113 samples was identified where calibrated PSL was also available. Drawing on routine analysis conducted at SUERC since 2001 a further set of 554 samples with PSL screening and TL data has also been considered. Qualitative correspondence has been cross-tabulated, confirming the existence of data sets where PSL screening outcomes and TL analytical outcomes diverge. Quantitative analysis of the sensitivities of both PSL and TL, where available, and the outcomes confirms that lack of luminescence sensitivity, coupled to a low concentration of irradiated material in a mixture accounts for many of these cases. Other scenarios where PSL may be detecting irradiated materials present in water-soluble or acid-soluble phases that are not present in TL samples have also been considered, as has the possibility that samples with high geological residual signals might mask TL detection of minor irradiated components.

The data sets accumulated provide a context for selection of samples for investigation of pre-concentration and serve as a reference for later parts of the project.

1. Introduction

Photo-stimulated luminescence (PSL) and thermoluminescence (TL) methods for detection of irradiated food (using standards EN1788[7] and EN13751[8] respectively) were initially developed for herbs and spices, but have subsequently been extended to a number of other product categories, such as shellfish. Validation studies[4] have been conducted on many of these, but in principle the methods can be applied to any foods containing silicate minerals. Dietary (herbal) supplements are among the products covered by the provisions of the Food Safety Act[19] unless they are clearly medicinal products for the treatment or prevention of disease. Therefore labelling regulations apply and detection of undeclared irradiation is an issue. Use of luminescence detection techniques over a number of years both by industry and in government surveys has led to a belief that there is a significant number of apparent mis-matches in classification when more than one of the techniques is used. This project aims to assess whether the incidence of mis-match is in fact significant, and also to understand why such outcomes arise and to investigate methods of reducing the incidence.

Photo-stimulated luminescence was developed as a screening test to identify samples which require further analysis by a method which takes account of sensitivity to ionising radiation, such as calibrated PSL (calPSL) or TL[1-4]. Extensive experience (in relation to herbs, spices, shellfish, fruit and vegetables) from validation studies[4], FSA project E01068 to develop a proficiency testing scheme for these methods[5], and more than 3000 commercial analyses performed at SUERC since 1996 shows that in most instances (more than 95%) where this procedure is followed, the two techniques are in agreement, but with dilute mixtures or materials with low mineral load it has been occasionally observed that TL evidence of irradiation can occur in conjunction with negative PSL. There are also cases of non-negative PSL signals which are not associated with TL evidence of irradiation, but these are rarer still.

Extension of the techniques to materials other than those originally subjected to inter-laboratory trials appears to have increased the incidence of such mis-matches, as does increased blending. In particular, dietary supplements, which are often either multi-ingredient and/or contain highly processed extracts with few minerals, but which have been found[6] to be frequently irradiated, require further study.

Apparent mis-matches arise when positive or intermediate PSL screening of a sample leads to further investigation by TL which does not reveal an irradiated component, or where positive TL analysis is associated with negative PSL. Such outcomes have been observed in commercial samples analysed at SUERC and also in surveys. Commercial submissions with negative PSL are not often referred for TL, so instances of the second form of discrepancy are largely confined to survey evidence, where TL analysis of a random selection of samples giving negative PSL has been performed. It should not, however, be assumed that TL is always correct in such instances, since there are circumstances, such as the presence of water-soluble PSL-bearing salts or large geological signals, where a positive PSL will be correct even when not corroborated by TL. Therefore, apparent mis-matches should be examined on a case by case basis.

Where TL is not associated with a PSL signal, the cause may be low sensitivity, dilution of the irradiated component by blending, loss of PSL signal, or physical form of sample.
An investigation[20] was undertaken in 1999 to study the impact of blending on herbs and spices. Sensitivity variation was also incorporated into the study protocol. A total of 162 blended samples was produced for analysis. Standardised and validated procedures were used for all analyses. As expected, detection rates were lower for diluter or less sensitive materials. At 10% concentration, PSL detection rate was 100% and TL 98%. At 1% concentration, PSL detection rate was 68% and TL 75%. At 0.1% concentration, PSL detection rate was 33% and TL 54%.

This demonstrates that there is a significant possibility of non- detection for both PSL and TL methods at low concentration and that there is a difference between PSL and TL detection rates at any given concentration. When assessing mis-matches, the possibility of blending therefore needs to be taken into account, particularly where sensitivity is likely to be low.

The work described below includes the initial identification of existing data sets at SUERC which contain dietary supplements, review of these data sets, examination of PSL versus TL outcomes, and of sample groups/types associated with different PSL screening and TL outcomes. This report also summarises these investigations and potential future work.

2. Review of existing data sets including dietary supplements which have been analysed with PSL, calPSL and TL.

As a first step, luminescence data from dietary supplements available at SUERC have been identified. Data sets reviewed included surveys conducted by SUERC between 2001 and 2005 for the Food Standards Agency[6,9], for National Authorities in Ireland, Denmark and Norway, and for a consortium of European Consumer Organisations, as well as samples routinely examined in response to individual submissions from other organisations between 2001 and 2008.

The surveys together comprised 1007 analyses, of which 427 were from dietary supplement samples. Of these, 280 samples had both PSL screening and TL analysis. Full calibrated PSL data sets in combination with TL analysis were available for 113 of these samples. These data sets have been examined in detail in this study. Both qualitative and quantitative descriptive analyses are presented below, with full details at the level of individual samples presented in Appendices.

Between 2001 and 2008 routine analyses were performed from 7967 samples, of which 5182 were classified as dietary supplements and their excipients. Normally these would have been submitted to SUERC for either PSL screening analysis or for TL analysis. The combination of PSL screening and TL analytical data exists in our database for 554 samples. The qualitative correspondence between PSL screening outcomes and TL outcomes has been reviewed for these cases.

2.1 Identification of data sets

Ten data sets from the surveys, which included dietary supplements, were identified as summarised below. Where these also contained other materials, that has been noted, together with the total number of samples submitted in each product category. The techniques used are also tabulated for each of these surveys.

Number	Submitting body	Date	Samples	Techniques
1	UK Food Standards Agency	2001/2	Herbs and spices (203), shellfish (202), dietary supplements (138)	PSL, calPSL and TL
2	UK Food Standards Agency	2003	Dietary supplements (47)	PSL, calPSL and TL
3	Food Safety Authority of Ireland	2002	Dietary supplements (24)	PSL and TL
4	Food Safety Authority of Ireland	2003	Dietary supplements (26)	PSL and TL
5	Food Safety Authority of Ireland	2005	Dietary supplements (20)	PSL and TL
6	Norwegian Food Safety Authority	2003/4	Herbs and spices (10), shellfish (10), dietary supplements (10)	PSL, calPSL and TL
7	Norwegian Food Safety Authority	2004/5	Shellfish (13), dietary supplements (21)	PSL, calPSL and TL
8	Danish Veterinary and Food Administration	2003	Dietary supplements (40)	PSL and TL
9	Danish Veterinary and Food Administration	2005	Dietary supplements (22)	PSL and TL
10	Belgian Food Commission (samples from Belgium, Italy, Spain and Portugal)	2004	Herbs and spices (79), shellfish (65), dietary supplements (79)	PSL and TL

Table 2.1: Summary of surveys examined in this project

The data sets reviewed thus comprised a total of 1007 samples of which 292 were herbs and spices, 290 were shellfish and 427 were dietary supplements. All samples were screened using PSL; for four of the surveys calPSL analyses were also

performed on all samples, giving a total of 216 dietary supplement cases where PSL sensitivity could be considered along with the outcomes of PSL screening. Of these 113 samples were also passed on to TL analysis. The surveys examined comprise 2 conducted by the UK Food Standards Agency[6,9], 3 for the Food Safety Authority of Ireland[10-12], 2 each for the Norwegian Food Safety Authority[13-14]and the Danish Veterinary and Food Administration, Regional Veterinary and Food Control Authority[15-16] and also one organised by the Belgian Consumer Association with samples submitted by equivalent bodies in Italy, Spain and Portugal as well as Belgium[17]

The selection criterion for progressing to TL varied from survey to survey. In all of the studies samples with intermediate or positive PSL progressed to TL analysis. In the FSA studies 10% of samples with negative PSL screening outcomes were also selected for TL analysis. In the Irish studies [10-12], all samples underwent TL analysis. In the Danish studies[15-16] samples had been pre-screened using the DEFT/APC method, and were then submitted for TL analysis; PSL analyses being conducted informally by SUERC at the same time. The PSL outcomes of samples which were not selected by DEFT/APC are unknown.

For both the FSA surveys, samples were purchased by Trading Standards Officers in 5 regions of the UK (Yorkshire, Oxfordshire, Wales, Northern Ireland, Scotland) according to an explicit schedule. 138 dietary supplements were purchased out of a total of 543 samples in 200 product categories in 2001. Following the discovery that of the dietary supplement samples analysed, 44 were identified as being irradiated and 14 as containing an irradiated ingredient. This lead to a follow-up survey in 2003, conducted again under enforcement conditions, looking at the same products where possible. 47 products were purchased by Trading Standards Officers, and analysed at SUERC.

The Food Safety Authority of Ireland also conducted surveys on dietary supplements prompted by the high incidence of irradiation of herbal supplements in the FSA 2001/2 survey. Twenty-four herbal supplements were bought “off the shelf” from health stores, a supermarket and a pharmacy. These herbal supplements were in either capsule or tablet form. Both PSL and TL methods were used for the analysis of these samples. Ten of the 24 samples had either been irradiated (4) or contained and irradiated component (6).

In the second Irish survey, twenty-six herbal supplements and substances were purchased “off the shelf”. Again, the herbal supplements were in capsule or tablet form. All samples underwent both PSL screening and TL analyses. Ten of the samples tested were described as “herbal substances” because they were presented for sale as powders or in leaf form rather than as packaged doses. 13 of the 26 samples tested were found to have been irradiated: a total of 11 of the 16 herbal supplements (5 irradiated and 6 containing an irradiated component) and 2 of the 10 herbal substances, both containing an irradiated component.

A further Irish survey targeting herbal supplements that had previously been shown to be either irradiated or to have an irradiated component was carried out in 2005. A total of 20 herbal products were purchased “off the shelf”. Of the 23 samples that were identified as having been irradiated in previous surveys five were unavailable

(discontinued or out of stock) and therefore two extra herbal supplements were included. The products included both supplements and substances. No distinction was made between these categories in the FSAI's final report. Of the eight products previously identified as irradiated in both 2002 and 2003, four of these were again found to be irradiated, three contained an irradiated component and one was negative. Of the 11 products identified as having an irradiated component in 2002 and 2003, one was irradiated and the remainder contained irradiated components.

Two surveys in Denmark were prompted by the FSA disclosure that unlabelled irradiated dietary supplements were to be found in the UK market. In 2003 106 herbal food supplements (either capsules, tablets or powder) were identified as being worthy of examination and examples of each were purchased by the 11 Danish Regional Laboratories, from the importer or manufacturer where possible[18].
All 106 products were screened using DEFT/APC. 40 samples had a DEFT/APC log difference of 4.0 or greater, defined in EN13783[21] as indicating irradiation. These 40 samples were then analysed using both PSL and TL at SUERC, leading to 5 positive, 6 intermediate and 28 negative PSL screening results. All these samples also underwent TL analysis, leading to 15 irradiated results (11 positive and 4 containing irradiated components). This was interpreted [18] as evidence that DEFT/APC produces a lot of "false positives", but since due to study protocol it was not possible to compare luminescence analyses with negative DEFT/APC, the incidence of "false negatives" cannot be assessed here. It was also observed that some clean products and/or those with only minor irradiated ingredients produced TL signals associated with negative PSL

In a follow-up survey in 2005, 22 samples were submitted to SUERC for analysis. Sample types corresponded to those in the earlier survey. PSL screening showed that 21 of these samples were negative and one was intermediate. TL was performed on all 22 samples, with 16 negative outcomes, 4 positives and 2 containing irradiated components. .

Small numbers of samples (10 and 21 respectively) were examined in two Norwegian government surveys in 2003 and 2004. Only those samples with non-negative PSL were progressed to TL, 12 samples in total; there were no random negatives selected for this survey.

Four EU countries (Belgium, Italy, Spain and Portugal) provided samples for an investigation co-ordinated by the Belgian Consumer Association in 2003. Herbs, spices and shellfish were examined as well as 79 dietary supplements. Instructions for purchase were provided for collaborators in each country. The samples were either capsules, tablets or tea bags. Only those samples with non-negative PSL were progressed to TL, no random 10% of negative PSL screening were put forward for TL.

As indicated above, not all surveys use all 3 techniques, and the selection criteria for the studies may introduce some elements of bias relative to the full range of marketed product.

An initial examination of PSL screening correspondence with TL outcome was performed to identify cases where mismatched outcomes were obtained. The incidence of negative PSL outcome followed by TL identification of irradiated components was represented by 44 samples from the 280 (15.7%); whereas 19 samples (6.8%) were observed where negative PSL screening was followed by a wholly positive TL results. This suggests that PSL screening may be lacking power relative to TL analysis in cases where low sensitivities are coupled to low concentrations of irradiated ingredients in compound products. It was noted that the incidence of these cases in the smaller survey studies was greater than in the initial FSA work, which is believed to be linked to the types of samples selected, not all of which had high mineral contents.

The less well recognised combination of positive PSL screening outcome coupled to a negative TL result is represented by 6 samples from the 280 survey examples (2%) of cases. Table B.1, in appendix B summarises the outcomes of each survey, and numbers of mismatched outcomes, followed tabulations of the individual identities of such samples from the first 5 surveys.

From the 554 samples identified from routine analyses of dietary supplements the negative PSL /positive TL category has a similar incidence of 46 examples (8%); while negative PSL outcomes were followed by TL identification of irradiated components in 49 cases (9%). The incidence of positive PSL followed by negative TL is 13 samples (2%). These percentages seem to be similar to those observed in survey data sets.

2.2 Qualitative examination of PSL and TL outcomes

Prior to examining the qualitative outcomes in further detail data were extracted from the survey records and a spreadsheet assembled containing the sample descriptions, PSL screening and (where available) calibrated PSL data and outcomes, TL glow 1 and glow 2 intensities, G1/G2 ratios, G1 peak descriptions where relevant, and the TL outcome. This has been used for both qualitative and quantitative examination of the patterns of correspondence and mismatch between PSL and TL.

For the qualitative description both PSL and TL have three potential outcomes. PSL screening results are classified into the 3 EN13751 screening bands on “negative”, “intermediate”, and “positive”, defined by signal intensity relative to the 2 standard theshold levels. TL outcomes have also been considered in three categories. Negative TL outcomes are from samples with low glow ratios and no evidence of a low temperature peak in the first glow TL signal. Positive TL outcomes are associated with the high glow ratios typical of pure irradiated materials, invariably accompanied by low temperature TL glow peaks in first glow. The third category is where samples exhibiting significant low temperature TL peaks in first glow have low TL glow ratios. These are identified as containing irradiated components. Depending on the relative luminescence sensitivities of ingredients in a compound food product the glow ratio might be considered as a first-order proxy for concentration of the irradiated component. The 9 permutations of PSL and TL outcome have been tabulated, so that the PSL-TL correspondence can be examined further. Tables 2a and 2b display the total number of samples in each of the possible PSL/TL

combinations (negative/negative, negative/component etc) for the full data set and the sub-set where calPSL was performed respectively.

	TL		
PSL	Negative	Component	Positive
Negative	72 (26%)	45 (16%)	19(7%)
Intermediate	23(8%)	14(5%)	22(8%)
Positive	6(2%)	6(2%)	73(26%)

Table 2.2. Comparison of PSL and TL outcomes for 280 dietary supplement samples from survey data

From Table 2.2 it can be seen that the majority of samples are either negative/negative (26% of total) or positive/positive (also 26% of total) and that where a negative PSL result is associated with a non-negative TL outcome, most show components (16% of total) rather than being fully positive (7%). Intermediate PSL leads to equal percentages (8%) of negative and positive TL, with a further 5% showing components; one and a half times as many samples with intermediate PSL show some evidence of irradiation as do not. For positive PSL, 2% of the total number of samples have negative TL. A further 2% have evidence of a component.

From these figures it can be seen that with this particular data-set, 64 samples out of 280 with TL evidence of the presence of irradiated material do not display PSL signals which would lead to further analysis as recommended by EN13751. 115 samples would have been selected for further investigation. In contrast, only 6 samples with positive PSL and 23 with intermediate PSL failed to show TL evidence of irradiated material. A further 6 samples with positive PSL showed evidence of an irradiated component.

	TL		
PSL	Negative	Component	Positive
Negative	19(17%)	16(14%)	6(5%)
Intermediate	4(4%)	5(4%)	11(10%)
Positive	4(4%)	4(4%)	44(39%)

Table 2.3. Comparison of PSL and TL outcomes for 113 dietary supplement samples from survey data where CalPSL data are available

Table 2.3 displays the same summary for the subset of 113 samples where calibrated data were also available. For these samples it will therefore be possible to examine the extent to which PSL sensitivity may provide an explanatory factor for cases where negative PSL screening has been followed by positive TL outcomes. Similar proportions of the negative PSL/TL component (14% cf 16% for the full data set) and negative PSL/positive TL combinations (5% cf 7%) were observed here. Slightly more of these samples give concordant PSL/TL data. The identities of the samples in these matrices are listed in Appendix A.

	TL		
PSL	Negative	Component	Positive
Negative	124 (22%)	49 (9%)	46 (8%)
Intermediate	73 (13%)	39 (7%)	69 (12%)
Positive	13 (2%)	13 (2%)	128 (23%)

Table 2.4. Comparison of PSL and TL outcomes for 554 dietary supplement samples from routine analysis

Table 2.4 shows the comparable distributions from 554 routine analyses of dietary supplements and their ingredients from 2001 to the present. In these cases PSL sensitivity has not been determined using the calPSL method; however it can be seen that the distributions across the outcome combinations are broadly similar to those from the survey data sets, with slightly more samples in the intermediate/positive category from routine analysis and slightly fewer in the negative/negative and positive/positive categories in a population with a generally higher incidence of non-negative samples.

Both these distributions, however, diverge from the long-term experience with pure reference products analysed under controlled conditions[4,5] such as herbs and spices, and with routine analytical experience from herbs and spices where PSL-TL correspondence where very few mis-matches are expected, and PSL screening is expected to identify more than 95% of irradiated products. . This may be a reflective of systematic differences between dietary supplements and their ingredients in comparison with most herbs and spices in terms of mineral contentrs, luminescence sensitivities, processing conditions (including purification of herbal extracts) and concentrations of herbal ingredients in composite products such as tablets or capsules. With multi-ingredient products, the constituents may have varying sensitivity as well as different concentration in the end-product, leading to heterogeneity. In cases where PSL fails to detect irradiated material which has been subsequently picked up in TL analysis it is of interest to explore whether this is associated with low mineral contents or sensitivities, or might be more linked to loss of PSL signals by fading or light exposure post-treatment. If the former, preconcentration of minerals from PSL samples might be helpful, which will explored later in the project, as will the possibility of utilising PSL depletion rates to assess the extent of light exposure prior to analysis. In cases where TL analysis fails to corroborate PSL screening two scenarios might be envisaged. If the PSL signal is due to a water or acid soluble phase in the sample, there is a possibility that the TL result is questionable. The other possibility is that the PSL signal arises from geological radiation exposure of the mineral content. A quantitative examination of the PSL and TL signal levels associated with the outcome combinations tabulated above may therefore be helpful in exploring these associations.

2.3 Quantitative summary data for each PSL and TL category

Tables 2.5 and 2.6 present summary statistics for the luminescence data for each of the outcome combinations tabulated above. Logarithmic intensities have been used, following the practice of the recent Proficiency Testing project[5]. Linear mean and standard deviations have been evaluated for PSL screening intensities (from the 280 survey samples where both PSL and TL data are available), calPSL intensities (for the 113 samples where these were available), mean G1 and G2 intensities for all samples where TL was carried out, and the mean glow ratios and mean log glow ratios for all these samples.

Tables 2.5 and 2.6 provide some insights into the role of sensitivity. Log-signal intensities for PSL and TL vary from approximately 2.5 to 6.6; noting that PSL intensities are constrained by the instrumental pre-load count of 256 to start at log 2.4, and that PSL screening intensities and calibrated PSL sensitivities progress systematically as the PSL screening outcome moves from "negative" through "intermediate" to "positive".

TL sensitivities also rise (from 4, to 5 , to 6) passing through the three PSL categories, but it is notable that the smallest value (log cycle 4) is more than 2 orders of magnitude greater than TL detection limits, even for those sample groups with the lowest PSL sensitivity. Thus it is evident that the mineral separation used in TL analysis has successfully enhanced signal to background ratios in comparison with un-treated PSL samples.

With a mean value of 3 log cycles (1000 counts) calibrated PSL sensitivity is lowest in the PSL negative/ TL positive group – which might also suggest that lack of PSL sensitivity could be an important factor for samples with this combination of outcomes. Clearly such low sensitivity PSL samples would fall into the negative screening band if signal losses due to post-irradiation fading, or to optical bleaching occurred. Calibrated PSL responses for the PSL-intermediate, and PSL-positive groups are significantly greater – up to 5 or more log cycles. Interestingly whereas the PSL-positive/TL-positive group has 4.9 log cycles of sensitivity; the PSL-positive/TL negative group, where interference with residual geological PSL signals is suspected, has the greatest mean PSL sensitivity (5.5 log cycles) of any of these groups.

TL sensitivity as measured by G2 intensity is higher for PSL-positive samples than for PSL-negative cases. Again the group for which geological interference is suspected (PSL-positive/TL-negative) has the highest TL sensitivity, suggesting that samples in this combination has the highest and most sensitive mineral loads of any group. It is unclear whether the presence of a high proportion of unirradiated minerals on a sample has a significant masking effect on the ability of the TL method to identify minor irradiated components. The data do however confirm that samples with 5-6 orders of magnitude PSL and TL sensitivities can produce positive screening outcomes, while TL analysis shows only geological glow shapes. As part of the review the original glow curves have been examined. None of the 6 samples in the PSL-positive/TL negative group show low temperature TL peaks, while all have relatively strong geological TL signals peaking in the 290-400°C region.

PSL		TL		
		Negative	Component	Positive
Negative	Mean log PSL*	2.48 ± 0.13	2.47 ± 0.14	2.47 ± 0.17
	Mean log CalPSL**	3.68 ± 0.77	3.86 ± 0.77	3.08 ± 0.20
	Mean log G1	3.58 ± 1.03	3.31 ± 0.69	4.21 ± 1.16
	Mean log G2	4.91 ± 1.31	5.01 ± 1.02	4.32 ± 0.95
	Mean G1/G2	0.09 ± 0.50	0.11 ± 0.36	1.44 ± 1.52
	Mean log G1/G2	-2.02 ± 0.84	-1.67 ± 0.72	-0.11 ± 0.53
Intermediate	Mean log PSL*	3.04 ± 0.30	3.03 ± 0.23	3.28 ± 0.30
	Mean log CalPSL**	4.30 ± 0.55	4.74 ± 0.38	3.78 ± 0.43
	Mean log G1	3.55 ± 1.02	3.52 ± 0.94	5.11 ± 1.27
	Mean log G2	5.80 ± 1.13	4.73 ± 1.16	5.08 ± 1.07
	Mean G1/G2	0.01 ± 0.01	0.12 ± 0.14	1.87 ± 1.87
	Mean log G1/G2	-2.30 ±0.76	-1.25 ± 0.66	0.02 ± 0.54
Positive	Mean log PSL*	3.93 ± 0.09	4.03 ± 0.43	4.80 ± 0.76
	Mean log CalPSL**	5.51 ± 0.28	4.91 ± 0.71	4.91 ± 0.59
	Mean log G1	4.98 ± 0.73	4.59 ± 0.73	6.17 ± 1.03
	Mean log G2	6.64 ± 0.81	5.98 ± 1.05	5.94 ± 0.98
	Mean G1/G2	0.03 ± 0.07	0.26 ± 0.69	2.15 ±1.81
	Mean log G1/G2	-2.08 ± 0.72	-1.42 ± 0.78	0.22 ± 0.34

* includes all samples for which TL was also performed

** subset of these samples for which calPSL was performed

Table 2.5 Summary statistics for all 280 survey samples classified by PSL/TL category

Mean G1 TL intensity integrated between 220-240°C is unsurprisingly higher in positive samples. For samples with components, however, the G1 mean is slightly lower than observed for the negative samples. The difference is not large but may be associated with sensitivity variation, particularly in blends. The mean G2 intensities support the suggestion that mineral load and sensitivity affect the size of the PSL signal.

Glow ratio is one of the EN1788 criteria for classifying samples, so the increase in this parameter with TL category is inevitable. There is also an increase with PSL signal, suggesting that this is a reasonably good predictor.

(Appendix A contains tables for each of the ten surveys separately, showing the distribution of products in each category, but without identifying mis-matches.

Appendix B summarizes the number and nature of the mis-matches and begins to examine the possible role of sensitivity in this.)

PSL		TL		
		Negative	Component	Positive
Negative	Mean log PSL	2.52 ± 0.11	2.53 ± 0.19	2.47 ± 0.17
	Mean log CalPSL	3.68 ± 0.77	3.86 ± 0.77	3.08 ± 0.20
	Mean log G1	3.11 ± 1.00	3.30 ± 0.63	4.87 ± 1.54
	Mean log G2	5.10 ± 1.42	4.96 ± 0.96	4.99 ± 1.32
	Mean log G1/G2	-2.01 ± 0.95	-1.66 ± 0.68	-0.13 ± 0.56
Intermediate	Mean log PSL	2.98 ± 0.38	3.14 ± 0.21	3.35 ± 0.22
	Mean log CalPSL	4.30 ± 0.55	4.90 ± 0.26	3.78 ± 0.43
	Mean log G1	1.91 ± 0.73	3.56 ± 1.13	5.36 ± 0.97
	Mean log G2	4.12 ± 0.70	4.56 ± 1.23	5.10 ± 0.94
	Mean log G1/G2	-2.25 ± 1.40	-1.21 ± 0.46	0.27 ± 0.49
Positive	Mean log PSL	3.68 ± 0.24	4.06 ± 0.53	4.71 ± 0.58
	Mean log CalPSL	5.48 ± 0.28	4.95 ± 0.71	4.89 ± 0.59
	Mean log G1	4.90 ± 0.88	4.49 ± 0.75	5.98 ± 1.12
	Mean log G2	6.61 ± .081	5.70 ± 0.96	5.77 ± 1.07
	Mean log G1/G2	-1.71 ± 0.22	-1.25 ± 0.83	0.21 ± 0.39

Table 2.6. Summary statistics for 113 survey samples with calPSL, classified by PSL/TL category

2.4 Graphical analysis of PSL and TL correspondence

The following section presents the survey data in graphical form, from which additional detail can be seen. Bearing in mind that both PSL and TL analyses are conducted on separate subsamples, and it is interesting when considering the possibility that pre-concentration of PSL samples might improve PSL sensitivities, before considering the relationships between PSL and TL further concordance diagrams for the PSL data have been prepared. These are shown in figure 2.1, which correlates the PSL signals from paired aliquots both in the screening data and in the calibrated PSL measurements. In both cases signals range over 4 orders of magnitude with good correspondence between aliquots. Whilst it might have been expected that the screening measurements would have been subject to greater dispersion, since these signals are in some cases due to heterogeneous mixtures of irradiated and unirradiated components, the two data sets are rather similar to each other in this respect. Figure 2.1 thus gives an indication of the amount of subsampling variation to expect when comparing PSL and TL data.

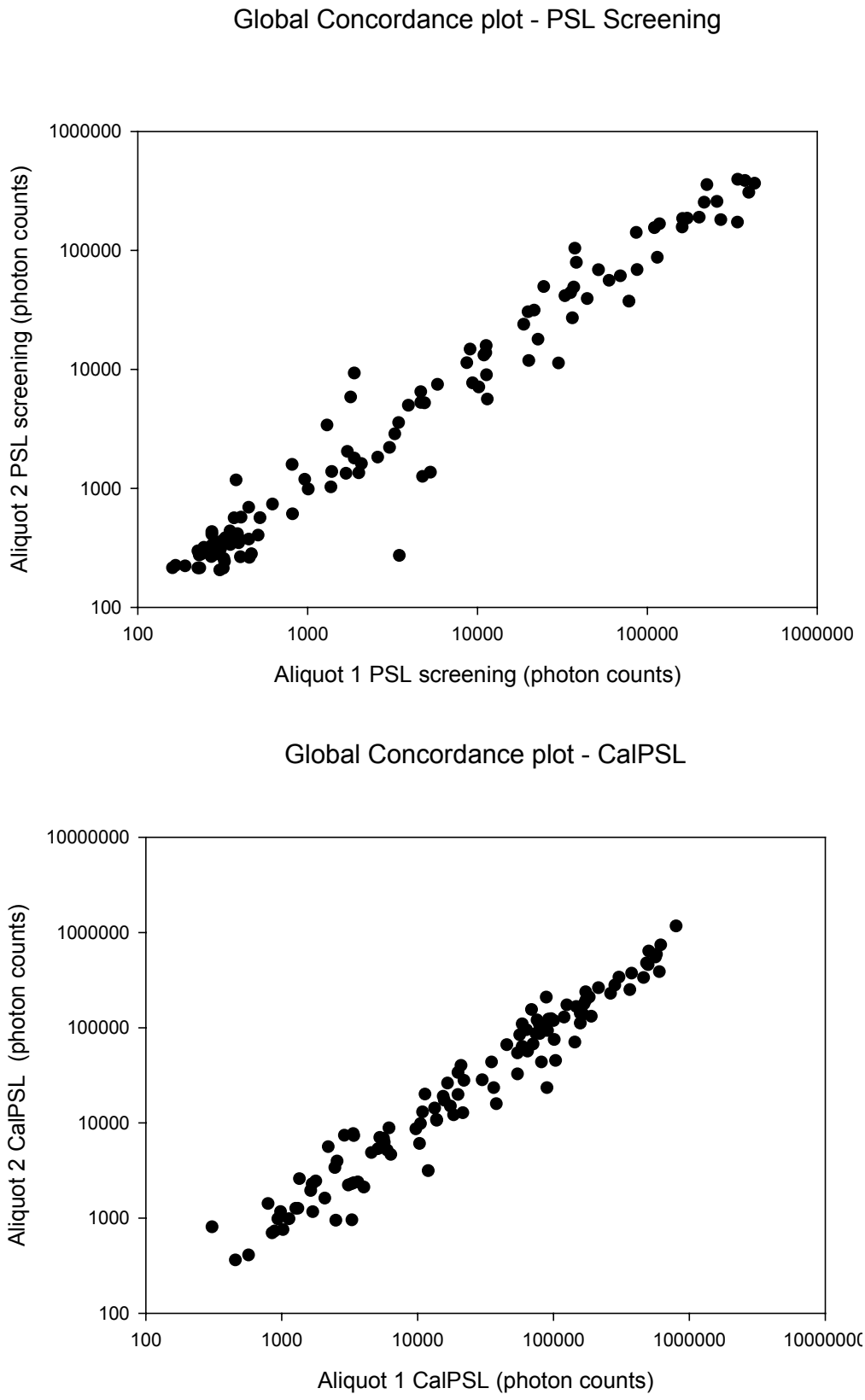

Figure 2.1 Concordance plot for all 4 surveys showing comparison between aliquots

Figure 2.2 shows calibrated PSL plots (calibrated PSL response plotted against initial PSL screening data) for all 113 samples for which calibrated PSL data are available. The upper plot shows data points covering both the domains of irradiated samples, and the parts of this plot where unirradiated and dilute mixtures would be expected. The lower plot identifies the PSL-TL outcome subgroups as distinct symbols.

Looking at the domain of irradiated samples first, it is evident that the PSL-positive/TL positive samples (indicated as red squares) are all samples with relatively high PSL sensitivities which are clearly identifiable as irradiated on the basis of calibrated PSL as well as the PSL screening and TL outcomes. The majority of the samples with PSL-intermediate/TL positive outcomes (indicated as purple diamonds) also fall onto the low-sensitivity extension of the irradiated sample domain in the calibrated PSL plot (the diagonal axis of the plot). These would therefore appear to be samples whose PSL sensitivities have been inadequate to produce a PSL-positive band outcome, but which are essentially irradiated materials. A subset of this group (approximately 30%) however also falls above the diagonal axis. These samples thus appear to have a source of PSL sensitivity (according to the calibrated PSL response) which is not matched by the signals in their screening data. Either the PSL signals are unstable (to fading or bleaching), or, part of the calibrated PSL sensitivity is accounted for by unirradiated, water-soluble or acid-soluble, components which would not have been represented in the TL analysis. Other PSL-intermediate samples are associated with diverse TL outcomes, as would be expected.

PSL-Negative samples associated both with TL-component and TL-negative outcomes plot in the areas of the calibrated PSL plot associated with unirradiated samples and with samples containing dilute irradiated components. It has been noted before (indeed even within the EN13751 standard) that calibrated PSL data are unable, on their own, to resolve these two situations. It is also noted that the small number of PSL-negative/TL positive outcomes all plot in the extremity of the low-sensitivity limit of the diagonal axis ie where irradiated samples would lie. Clearly the PSL sensitivity in these cases was inadequate.

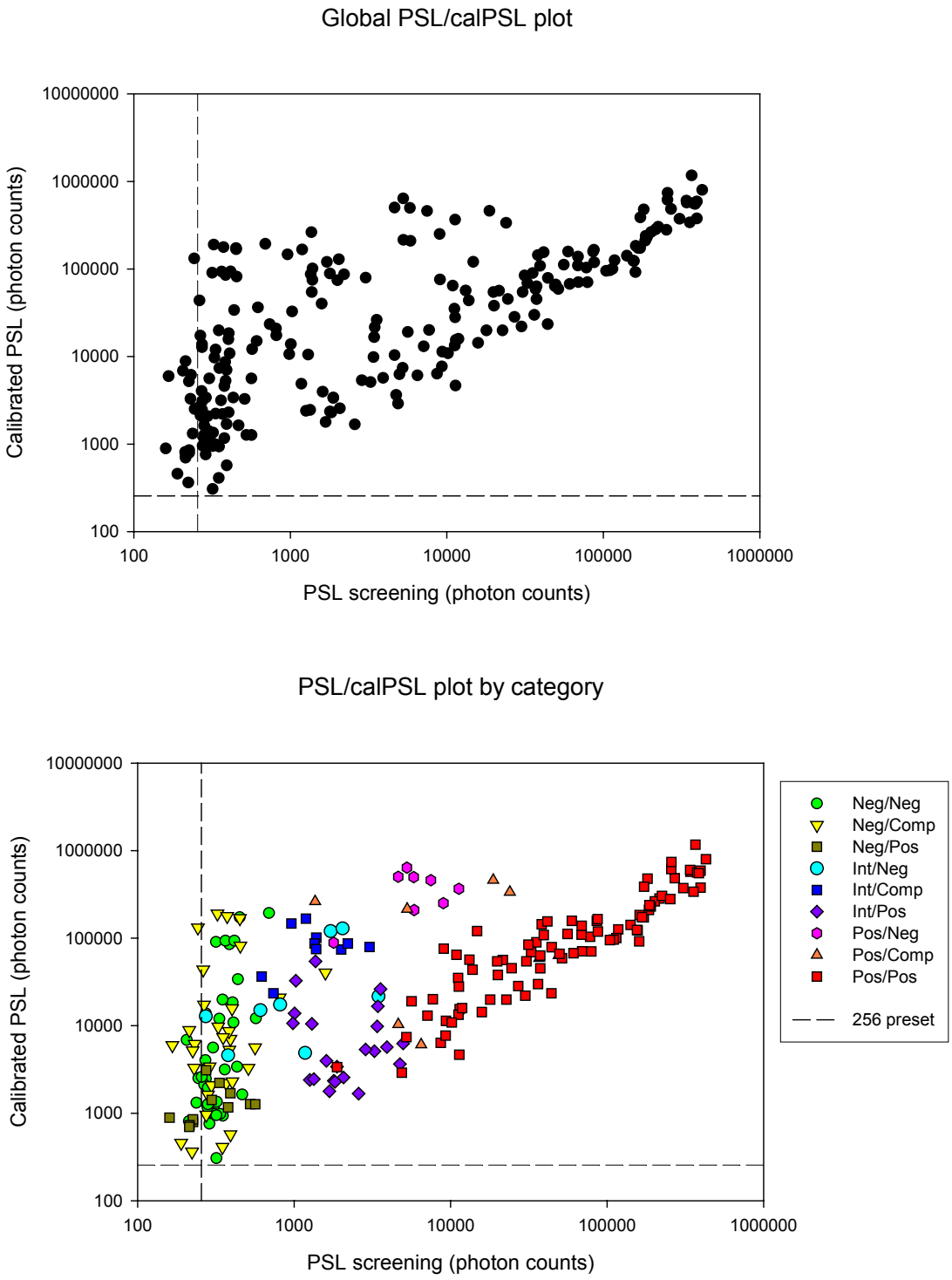

Figure 2.2. Calibrated PSL plot for 113 survey samples In both plots the 256 preset has been indicated by a dotted reference line.

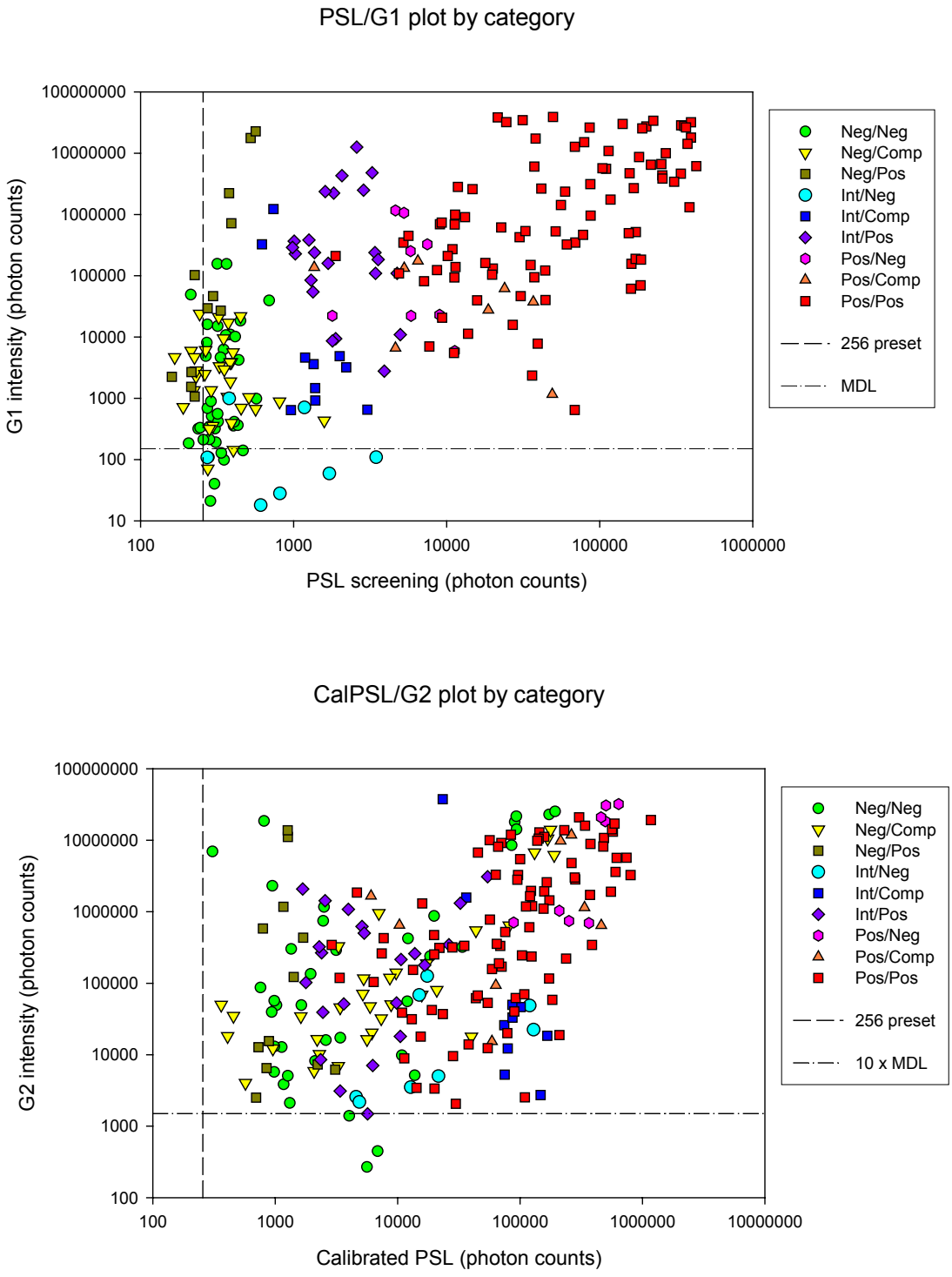

Figure 2.3 TL and PSL scatter plots **The 256 preset for PSL is shown by a dotted line and a notional 10 x MDL for G2 TL by a dot-dash line.**

Figure 2.3 compares PSL and TL signal strengths for the same materials: the upper plot compares PSL screening with TL G1 signal intensities. By analogy the lower plot compares calibrated PSL measurements with G2, thereby comparing sensitivity. In both plots the diagonal is a broad indicator of sample sensitivity. In the lower plot it represents direct measures of PSL and TL sensitivity, which are loosely correlated over 3-5 orders of magnitude.

In the upper plot sensitivity is also combined with the influence of the variations in initial PSL and TL signals, which of course carry indicators of prior irradiation and any geological residuals as well. The upper plot thus carries 4-6 orders of magnitude of variation. Off-axis samples in the upper plot indicate samples with a-typically greater TL than PSL, or vice versa. Concordant samples exhibiting irradiated materials (PSL-Positive/TL-positive, and PSL-Intermediate/TL-Component outcomes) tend to occupy the diagonal axis. By contrast the concordant PSL-negative/TL-negative group is dispersed both above and below the axis. Those samples in this group with greater relative PSL signals compared with TL might be samples where water-soluble or acid-soluble but PSL sensitive phases are present. Some of these may potentially include undetected irradiated materials. Samples where TL intensities exceed expectations based on PSL screening results may imply fading or bleaching of PSL; or in the lowest sensitivity cases perhaps lack of sufficient mineral contents for effective PSL screening. There are examples of such cases in the PSL-negative/TL positive, and in the PSL-intermediate/TL positive groups.

The lower plot in figure 2.3 displays a greater scatter and overlap between the categories. High G2 intensity is slightly more likely to be associated with high calPSL than with low, but calPSL can be associated with a wide range of TL intensities at any calPSL order of magnitude.

In figure 2.3, samples classified as having irradiated components occupy the same part of the PSL/TL space as would blends examined in the proficiency testing study[5] , suggesting that dilution is a significant explanatory factor for mis-matched outcomes. It has been shown[20] that both PSL and TL fail to detect some blends under controlled conditions, with the proportion of undetected blends increasing with increasing dilution. Below 0.1% neither technique finds more than one third to half of the samples containing irradiated material. Therefore materials with low proportions of irradiated material in an unirradiated matrix may be undetected by one or both of the methods; agreement between methods will be observed where both methods fail or succeed, but a mis-match will result when only one method does not detect the component, regardless of which method is the successful one.

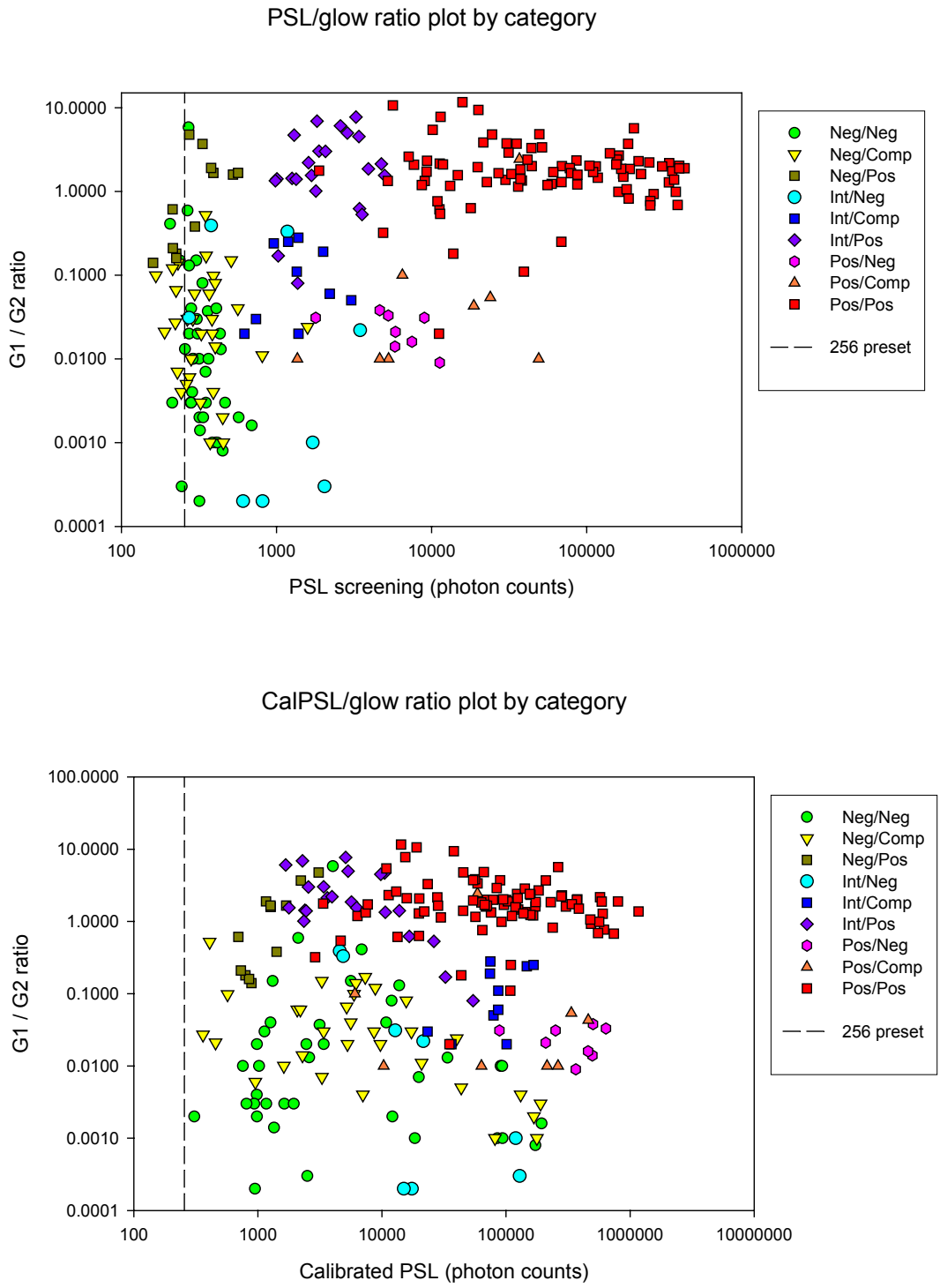

Figure 2.4 Comparison of PSL screening and calPSL with TL glow ratio

Figure 2.4 shows that samples with negative PSL screening and negative TL display a wide range of glow ratios, consistent with a spread of sensitivities in unirradiated materials. This is supported by the scattered distribution of these samples in the lower plot of calPSL versus glow ratio. A similar pattern is seen for samples with negative screening and TL evidence of an irradiated component, in both plots, possibly reflecting dominant sensitivity of the unirradiated portion of a mixture. All samples with negative PSL combined with positive TL show low PSL sensitivity in the lower

plot. However samples with negative PSL associated with TL detection of an irradiated component show a wide variation of PSL response, particularly at low glow ratios – where there is a suggestion of anticorrelation in the lower plot. This may reflect the difficulties in detecting low concentration blends by TL from samples with low sensitivities. Thus only from the highest sensitivity samples can low concentration blending be detected using TL. While this group shows diverse behaviour, and almost certainly comprises diverse product types, it is nonetheless arguable that sensitivity enhancement would be beneficial to extension of the analytical limits in both PSL and TL for these difficult cases.

Low glow ratios are observed for those samples with positive PSL screening but negative TL; all these samples have low positive PSL and in the lower plot can be seen to have high PSL sensitivity. This is consistent with natural geological signals detected by PSL. Positive PSL associated with irradiated components identified by TL is also associated with low glow ratios; the presence of a peak between 150°C and 250°C despite low ratios satisfies the EN1788 criteria for the presence of a component. These samples also have low positive PSL and relatively low PSL sensitivity. PSL-Intermediate/TL-Component outcomes are, perhaps unsurprisingly, associated with adequate PSL sensitivity, but lower glow ratios, than PSL-Intermediate/TL-Positive outcomes. Both upper and lower graphs in figure 2.4 confirm that, as expected, the high glow ratio samples with positive TL outcomes form a distinct and seemingly unambiguous group where both methods are generally in agreement.

3. Discussion

Having reviewed data sets from surveys including dietary supplements it has been possible to identify and explore the properties of cases where PSL and TL outcomes appear to diverge. The incidence of such cases is higher than expected from earlier experience of simple herbs and spices, but it has been noted that the dietary supplements are an extremely diverse product group including many examples with high dilutions of herbal ingredients and with highly processed forms. As well as the survey data sets, where 280 PSL screening/TL analysis combinations and 113 samples including calibrated PSL analysis could be examined, a further set of 554 samples was considered drawn from routine PSL and TL analysis.

In looking at these outcomes low sensitivity to PSL, and to a lesser extent to TL, emerges as an important factor in mismatched cases. Therefore development of effective techniques for pre-concentrating minerals in such products appears to be a justified and worthwhile step towards attempting to improve the performance of routine PSL screening for such materials.

It has also however been noted that there are samples and sample groups which seem to show unexpectedly low PSL signals when their PSL sensitivities and the associated TL outcomes are considered. The possibility that PSL instabilities or bleaching by exposure to daylight are associated with these cases cannot be excluded, and therefore sensitivity enhancement by pre-concentration may, for these cases, represent only a starting point to optimisation of the PSL method. Similarly a small number of cases was also observed where PSL appeared to detect signals which were not reproduced in TL analysis. The possibility that some of these are due to PSL carried by water-soluble or acid-soluble phases that would not find their way into routine EN1788 silicate preparations has also been noted. The other main scenario for obtaining a mis-match between initial screening outcome and subsequent TL analysis is where geological interference can produce a response, that is not subsequently shown to be associated with a low-temperature TL curve. Several instances of this behaviour were noted in the review – interestingly tending to come from high-sensitivity rather than low-sensitivity samples. The extent to which samples with high TL or PSL sensitivities from unirradiated minerals carrying geological residuals can mask the presence of less sensitive irradiated phases is at this stage unclear.

The next stages of this study are to develop preconcentration methods to enhance mineral content for PSL measurements. It is hoped that this will result in an immediate performance enhancement for those cases where insufficient sensitivity is the main reason for failure of PSL screening to detect irradiated material. The project also envisages examination of other PSL indicators of prior optical exposure and potentially geological signals, based on depletion rate analysis and signal ratios observed in two different stimulation wavelengths, where concentration or separation of minerals facilitates additional approaches to the analysis.

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Appendix A – Samples by Survey, PSL and TL outcome

	TL		
PSL	Negative	Component	Positive
Negative	1	5	1
Intermediate	2	2	9
Positive	1	2	32

	TL		
PSL	Negative	Component	Positive
Negative	SP4555 SawP	SP4595MilkT,SP4590Ginseng, SP4672Gingko,SP4940Aloe, SP5061Ginger	SP4771Aloe
Intermediate	SP4669Ginger, SP4926Gua	SP4537Gar,Sp4685Gar	*
Positive	SP4549GTea	SP4936Ginseng,SP5052Gingko	**

*	SP4546	Kava kava
	SP4776	Ginger
	SP4778	Kava kava
	SP4779	Saw palmetto
	SP4932	Kava kava
	SP4544	Ginger
	SP4547	Saw palmetto
	SP4773	Devil's claw
	SP4780	Cat's claw

**	SP4535	Ginseng
	SP4536	Ginseng
	SP4538	Alfalfa
	SP4539	Aloe Vera
	SP4543	Silymarin/Milk Thistle
	SP4550	Gingko biloba
	SP4554	Milk thistle
	SP4556	Ginseng
	SP4560	Guarana
	SP4564	Ginger
	SP4570	Garlic
	SP4571	Ginseng
	SP4573	Devil's claw
	SP4577	Garlic
	SP4581	Devil's claw
	SP4585	Turmeric
	SP4588	Cat's claw
	SP4666	Ginseng
	SP4682	Ginseng
	SP4768	Ginseng
	SP4772	Guarana
	SP4774	Gingko biloba
	SP4785	Ginseng
	SP4929	Silymarin/Milk Thistle
	SP5040	Devil's claw
	SP5042	Silymarin/Milk Thistle

SP5048	Ginseng
SP5049	Ginger
SP5059	Ginseng (Siberian)
SP5060	Ginseng (Ultra Manchurian)
SP5063	Cat's claw
SP5064	Cat's claw

Table A1. FSA 2001

	TL		
PSL	Negative	Component	Positive
Negative	18	8	4
Intermediate	1	0	1
Positive	3	2	8

	TL		
PSL	Negative	Component	Positive
Negative	*	**	***
Intermediate	SP6794Brain Food		SP6824Odourcontrolledgar
Positive	^	SP6821Concgar,SP6828Ginseng	^^

	*	SP06793	Ginkgo biloba leaf extract
		SP06795	Ginkgo biloba
		SP06799	Manchurian ginseng
		SP06800	Guarana
		SP06801	Guarana
		SP06810	Ginkgo biloba extract
		SP06817	Ginkgo biloba
		SP06825	Turmeric
		SP06826	Green Tea extract
		SP06827	Saw palmetto
		SP06785	Saw Palmetto
		SP06788	Turmeric root extract
		SP06796	Ginkgo biloba
		SP06797	Korean Ginseng
		SP06806	Ginger Root
		SP06808	Ginkgo
		SP06809	Aloe Vera Tablets
		SP06819	Alfalfa

**	SP06815	Saw palmetto
	SP06816	Ginkgo biloba

SP06802	Guarana seed
SP06814	Ginkgo biloba
SP06784	Saw Palmetto
SP06789	Turmeric
SP06798	Siberian Ginseng
SP06807	Ginger Root

***	SP06783	Saw Palmetto
	SP06803	Guarana
	SP06804	Siberian Ginseng
	SP06805	Korean Ginseng

^	SP06812	Siberian ginseng
	SP06813	Siberian Ginseng
	SP06820	Concentrated garlic

^^	SP06782	Super Alfalfa
	SP06786	Saw Palmetto complex with pygeum bark
	SP06787	Turmeric root extract
	SP06791	Aloe Vera
	SP06792	Aloe Vera
	SP06818	Alfalfa
	SP06823	Odourless garlic
	SP06829	Korean Ginseng

Table A2. FSA 2003

	TL		
PSL	Negative	Component	Positive
Negative	10	7	1
Intermediate	3	0	0
Positive	0	0	3

	TL		
PSL	Negative	Component	Positive
Negative	*	**	SP5977DongQ
Intermediate	^		
Positive			^^

*	SP05970	Black Cohosh
	SP05973	Camomile Herbal Tea
	SP05978	Echinacea
	SP05979	Echinacea Plus
	SP05982	Ginger
	SP05983	Ginseng
	SP05984	Korean Ginseng
	SP05986	Korean Ginseng
	SP05988	Guarana
	SP05989	Milk Thistle Extract

**	SP05972	Butcher's Broom
	SP05974	Devil's Claw
	SP05975	Devil's Claw
	SP05981	Unique Garlic
	SP05990	Silymarin/ Milk thistle
	SP05992	Saw Palmetto
	SP05993	Turmeric

^	SP05980	Concentrated Garlic
	SP05985	Ultra Ginseng
	SP05987	Siberian Ginseng

^^	SP05971	Black Cohosh
	SP05976	Devil's Claw
	SP05991	Raspberry Leaves

Table A3. FSAI 2002

	TL		
PSL	Negative	Component	Positive
Negative	9	6	1
Intermediate	2	1	2
Positive	1	1	2

	TL		
PSL	Negative	Component	Positive
Negative	*	**	SP6311Kyolicgar
Intermediate	SP6302Butchersbroom+oil, SP6318MilkT	SP6307DongQ	SP6298AgCast, SP6309Feverfew
Positive	SP6323Val	SP6310Gar	SP6299Aloe, SP6314SibGin

*	SP06301	Black Cohosh
	SP06303	Cat's claw tea bags
	SP06305	Devil's claw
	SP06306	Don Quai
	SP06315	Ginseng cut
	SP06317	Guarana Seed
	SP06319	Raspberry leaf
	SP06321	Skullcap
	SP06322	Strawberry leaves

**	SP06304	Cranberry concentrate
	SP06308	Effervescent Echinacea Extract
	SP06312	Ginger Root
	SP06313	Siberian Ginseng
	SP06316	Korean Ginseng
	SP06320	Saw palmetto

Table A4. FSAI 2003

	TL		
PSL	Negative	Component	Positive
Negative	1	11	4
Intermediate	1	2	1
Positive	0	0	0

	TL		
PSL	Negative	Component	Positive
Negative	SP365KGin	*	^
Intermediate	SP8348BlCoh	SP8353Effech,SP8363MilkT	SP8362SibGin
Positive			

*	SP08346	Aloe Vera
	SP08349	Devil's claw
	SP08350	Devil's claw
	SP08352	Dong Quai root
	SP08355	Unique garlic
	SP08356	Ginger root
	SP08357	Korean ginseng
	SP08358	Raspberry leaves
	SP08359	Saw palmetto
	SP08361	Siberian ginseng
	SP08364	Turmeric

**	SP08347	Aloe Vera superstrength tablets
	SP08351	Dong Quai
	SP08354	Kyolic garlic 1000
	SP08360	Saw palmetto extract

^	SP08347	Aloe Vera superstrength tablets
	SP08351	Dong Quai
	SP08354	Kyolic garlic 1000
	SP08360	Saw palmetto extract

Table A5. FSAI 2005

	TL		
PSL	Negative	Component	Positive
Negative	17	3	4
Intermediate	5	1	1
Positive	0	0	5

	TL		
PSL	Negative	Component	Positive
Negative	*	**	***
Intermediate	^	SP6453Evelle	SP6448Greenpills
Positive			^^

*	SP06449	PEP and TRIM, guarana
	SP06451	Traneboer tablet, cranberry
	SP06452	Garlic tablet
	SP06454	Ginkgo biloba extract
	SP06455	Ginseng extract
	SP06457	Hyben extract
	SP06459	Humle extract, hops extract
	SP06461	Dandelion extract
	SP06462	Thistle extract
	SP06463	Cynara scolymus
	SP06468	Ginseng pulv
	SP06471	Apple cider etc
	SP06472	Apple cider tablets
	SP06474	Cranberry tablet, vaccinium macrocarbon
	SP06476	Horsetail extract
	SP06477	Tomato extract
	SP06478	Cherry extract

**	SP06465	Melbrosia, flower pollen, royal jelly etc
	SP06466	Neolic, garlic capsules
	SP06480	Cats claw capsules

***	SP06460	Red clover extract
	SP06479	Aloe vera tablet
	SP06483	Guarana extract 16%

^	SP06447	All-zyme Double strength , orange, mango, carrot, ginger
	SP06450	Garlamin tablet, garlic etc
	SP06469	Marietidsel capsules, thistle

SP06470	Panax ginseng capsules
SP06486	Rhubarb root powder

^^	SP06467	Ingefeer rod, ginger
	SP06475	Prosansilica forte tablets
	SP06481	Guarana capsules
	SP06482	Pfaffia, pulv. Ginseng capsules
	SP06485	Horsetail powder

Table A6. Denmark 2003

	TL		
PSL	Negative	Component	Positive
Negative	16	2	3
Intermediate	0	0	1
Positive	0	0	0

	TL		
PSL	Negative	Component	Positive
Negative	*	SP8700Melbrosia,SP8713Solhat	**
Intermediate			SP8701GreenT
Positive			

*	SP08695	Rod Ginseng pulver
	SP08696	Serasee
	SP08697	Evelle
	SP08698	Neolic ekstra staerk
	SP08699	Melbrosia Plus
	SP08703	Colladerm
	SP08704	Kirsebaer ekstrakt
	SP08705	Agerpadderok ekstrakt
	SP08706	Tomatekstrakt
	SP08708	Solbaer ekstrakt
	SP08709	Gelle Royal ekstrakt 3:1
	SP08710	Ginseng Ekstrakt SD 4%
	SP08711	Birkeblads ekstrakt
	SP08712	Agerpadderok ekstrakt
	SP08714	Acerola ekstrakt 25%
	SP08716	Hybenpulver

**	SP08702	Agerpadderok ekstrakt 2%
	SP08707	Pep & Trim
	SP08715	Hvid te ekstrakt

Table A7. Denmark 2005

	TL		
PSL	Negative	Component	Positive
Negative	0	1	0
Intermediate	0	1	1
Positive	0	0	2

	TL		
PSL	Negative	Component	Positive
Negative		SP7303Ginger	
Intermediate		SP7301KorGin	SP7305Ginseng
Positive			SP7299Silica,SP730SibGin

Table A8. Norway 2003

	TL		
PSL	Negative	Component	Positive
Negative	0	1	1
Intermediate	1	2	0
Positive	0	0	2

	TL		
PSL	Negative	Component	Positive
Negative		SP8241Ingefar	SP8253Cran
Intermediate	SP8240Zinaxin	SP8238HairandSkin, SP8248KorGin	
Positive			SP8246Ginseng, SP8249Redclover

Table A9. Norway 2004

	TL		
PSL	Negative	Component	Positive
Negative	0	0	0
Intermediate	8	5	6
Positive	1	1	19

	TL		
PSL	Negative	Component	Positive
Negative			
Intermediate	*	**	***
Positive	SP7173Ech	SP7063Ech	^

*	SP06980	Juvaflorine- Ginseng propolis
	SP07064	Ginseng royal jelly

SP07068	Ginseng Vitality
SP07168	Ginseng - mat & diet
SP07178	Aglio Aboca
SP07225	Santiveri Ginkgo Biloba
SP07226	Solgar Ginkgo Biloba
SP07233	Santiveri Ajo

**	SP06986	Biover Echinacea, vit C and salva
	SP07052	Ginseng propolis guarana
	SP07065	Echinacea tablet
	SP07165	Ginseng - L'angelica (Guaber)
	SP07176	Aloe Ver Body Spring

***	SP06988	Argalys Tonico
	SP06994	Arkopharma Alho
	SP07053	Ginseng Forte Energie Vitalite
	SP07058	Cats Claw And Echinacea
	SP07220	Dolisos Jengibre
	SP07230	Resem Ginseng

^	SP06982	Vertnature Ginseng Kola
	SP06984	Sundown Ginseng Coreano
	SP06990	Rogoff Concentrated Extract Of Alho Forte
	SP07061	Echinacea arkogelules
	SP07067	Echinacea forte
	SP07069	Korean Ginseng Royal Jelly and Vit E
	SP07166	Ginseng - Cereal
	SP07174	Echniacea Body Spring
	SP07181	Guarana Natura e Benessere
	SP07214	Arkocapsulas Echinacea
	SP07215	El Clerigo Echinacea
	SP07216	Farmalia Echinacea
	SP07217	Intergralia Echinacea
	SP07218	Verdalia Echinacea
	SP07219	Arkocapsulas Jengibre
	SP07221	Verdalia Jengibre
	SP07224	Farmalia Ginkgo Biloba
	SP07228	Espsilon Ginseng
	SP07231	Santiveri Ginseng

Table A10. Belgian Consumer Association 2003

Appendix B– Summary tables of mis-matched outcomes

Survey Number	PSL outcomes	TL outcomes	Discrepancies
1	39P 17I 82N	44P 14C 7N	1 false P, 5 false N (C)
2	14P 3I 21N	12P 12C	3 false P, 1 false I, 11 false N (3P, 8C)
3	3P 3I 18N	4P 6C 13N 1I	3 false I, 7 false N (1P, 6C)
4	4P 6I 16N	5P 8C 12N 1I	1 false P, 2 false I, 6 false N (5C, 1N)
5	5I 15N	5P 13C 2N	2 false I, 15 false N (4P, 11C)
6	2P 2I 1N	3P 2C	2 false N (C)
7	2P 3I 16N	3P 3C	1 false I, 2 false N (1C, 1P)
8	5P 7I 27N	8P 4C 22N	5 false I, 5 false N (2P, 3C)
9	1I 21N	4P 2C 16N	5 false N (3P, 2C)
10	20P 20I	26P 5C 9N	1 false P, 9 false I

PSL : P=positive, I=intermediate, N=negative
TL : P=positive, C=component, N=negative, I=indeterminate
False positives, intermediates and negatives are defined as positive, intermediate and negative PSL results which are not corroborated by the TL analysis of the same material

Table B1: Summary of dietary supplement results in the ten surveys

FSA survey 2001/2

SP number	Description	PSL	Cal	TL
4549	Green tea	P	P	No LTP
4582	Gingko	N	P	LTP <0.1
4590	Ginseng	N	I/P	LTP <0.1
4672	Gingko	N	P	LTP <<0.1
4940	Aloe vera	N	P	LTP <0.1
5061	Ginger	N	P	LTP <0.1

LTP = low temperature peak
Figures are G1/G2

Table B2a: Mis-match results from the FSA 2001/2 survey

FSA survey 2003

SP number	Description	PSL	Cal	TL
6783	Saw palmetto	N	I	P
6784	Saw palmetto	N	P	C
6789	Turmeric capsules	N	P	P
6794	Brain food formula	I	P	N
6800	Guarana	N	I	C
6801	Guarana	N	I	P
6803	Guarana	N	P	C
6804	Siberian ginseng gel capsules	N	I	P
6805	Korean ginseng gel capsules	N	I	P
6807	Ginger root tablets	N	P	P
6812	Siberian ginseng tablets	P	P	N
6813	Siberian ginseng tablets	P	P	N
6814	Gingko	N	I	C
6815	Saw palmetto	N	N	C
6816	Gingko	N	N	C
6820	Garlic	P	P	N

Table B2b: Mis-match results from the FSA 2003 survey

FSAI 2002

SP number	Description	PSL	TL
5972	Butcher's broom root	N	C
5975	Devil's claw tablets	N	C
5977	Dong quai	N	P
5980	Garlic tablets	I	N
5981	Garlic tablets	N	C
5985	Ginseng capsules	I	N
5987	Siberian ginseng	I	N
5990	Silymarin milk thistle	N	C

5992	Good ‘n’ Natural	N	C
5993	Turmeric capsules	N	C

Table B2c: Mis-match results from the FSAI 2002 survey

FSAI 2003

SP number	Description	PSL	TL
6302	Butcher's broom	I	N
6304	Cranberry concentrate	N	C
6308	Effervescent echinacea	N	C
6311	Kyolic garlic 1000	N	P
6312	Ginger root	N	C
6316	Korean ginseng	N	C
6318	Milk thistle	I	N
6320	Saw palmetto	N	C
6323	Valerian root	P	N

TableB2d: Mis-match results from the FSAI 2003 survey

FSAI 2005

SP number	Description	PSL	TL
8346	Aloe vera	N	C
8347	Aloe vera	N	P
8348	Black cohosh	I	N
8349	Devil's claw	N	C
8350	Devil's claw	N	C
8351	Dong quai	N	P
8352	Dong quai	N	C
8354	Kyolic garlic	N	P
8355	Unique garlic	N	C
8356	Ginger root	N	C
8357	Korean ginseng	N	C
8358	Raspberry leaves	N	C
8359	Saw palmetto	N	C
8360	Saw palmetto	N	P
8361	Siberian ginseng	N	C
8364	Turmeric	N	C
8365	Korean ginseng	I	N

Table B2e: Mis-match results from the FSAI 2005 survey

	TL		
PSL	Negative	Component	Positive
Negative	20 (11 tablets, 6 capsules, 3 tea bags)	12 (6 tablets, 6 capsules)	6 (2 tablets, 4 capsules)
Intermediate	5 (3 tablets 2 capsules)	0	1 (pills)
Positive	3 (2 tablets, 1 capsules)	1 (capsules)	5 (2 tablets, 3 capsules)

Table B3 : Comparison of PSL/TL outcome with sample form for 53 samples where this is recorded.