Scottish Universities Environmental Research Centre

A PRELIMINARY INVESTIGATION OF THE IMPACT OF BLENDING ON LUMINESCENCE DETECTION OF IRRADIATED HERBS AND SPICES

PROJECT FS 1925

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SUMMARY

A preliminary investigation has been undertaken to study the impact of blending irradiated and unirradiated products on luminescence detection of irradiated herbs and spices. Samples of six products (oregano, basil, sage, paprika, ginger and cinnamon) were prepared combining irradiated material at three different concentration levels - 10%, 1% and 0.1% - with unirradiated product under controlled conditions. The luminescence sensitivities of both the irradiated and unirradiated products were varied systematically, producing 9 sensitivity combinations at each of the three concentration levels.

Samples were selected following an analysis of the sensitivity distributions of both PSL and TL from archival data sets at SURRC. Retained samples were combined under controlled conditions from materials believed to be unirradiated on the basis of previous PSL and TL analyses. Portions of these were irradiated to a 10 kGy gamma dose, and then recombined to produce the blended samples. Thus a total of 162 blended samples was produced for analysis. All samples were subjected to PSL screening measurements, and to TL analyses following standardised and validated procedures. The PSL analyses followed the draft EU standard method, which had been used in earlier MAFF supported interlaboratory trials. TL analyses were conducted relative to EN1788, and MAFF V27 protocols.

PSL screening results showed that all samples could be identified in either intermediate or positive bands in 10% concentration; the proportion detected falling to 68% of samples containing 1% irradiated material, and 33% of samples containing 0.1% concentrations. Signal strengths were generally higher for high sensitivity materials, as expected, although the low concentration blends showed high variations.

TL analyses were evaluated relative to both the 1998 revised EN1788 criteria, currently undergoing consultation prior to adoption, and to the 1996 criteria which form the current EN standard. The 1998 criteria, in keeping with MAFF V27 place emphasis on peak shapes, and recognise the possibility that glow ratios can be adversely affected by blending. When this is done 96% of samples with 10% irradiated material could be detected, falling to 75% with 1% irradiated material, and 54% with 0.1% concentrations. These figure compare favourably with those based on strict interpretation of the current (1996) EN1788 criteria where only 84%, 35% and 15% of these blends would have been identified as irradiated at the three respective concentration levels. These overall results confirm the importance of using peak shape as a primary classification tool, where blended materials are encountered. However when taken to critical limits this can introduce subjective elements to classification. Glow 1 peak shapes could be shown to comprise mixtures of two signal components - the higher temperature forms associated with residual geological luminescence in the silicate assemblages used for analysis, and the lower temperature components associated with the irradiated fractions. The data sets broadly confirm the expected behaviour of these components as a function of the sensitivities and concentrations of the irradiated components and the unirradiated matrices.

Overall it can be seen that standard methods are able to detect a significant proportion of irradiated blends at concentrations above 1-10%. Below these concentrations there is a significant probability of non-detection, particularly for low sensitivity components.

CONTENTS

1. Introduction

Project FS 1925 provides a preliminary investigation of the impact of blending on detection of irradiated herbs and spices using validated and standardised luminescence procedures.

Treatment with ionising radiation is an effective means of reducing microbial load without compromising product quality. For this reason herbs and spices are amongst the products most commonly irradiated in commercial plants. They are also products with diverse sources and a complex multinational supply and distribution chain. They are frequently subject to mixing, either by processes of consolidation of large batches of material from diverse production, or as a result of blending aimed at producing consistent qualities of flavour, colour or other attributes. As ingredients, herbs and spices are also used in seasonings, and in compound foods. For all these reasons irradiated herbs and spices can find their way into dilute mixtures in the food supply chain, presenting a different range of analytical problems from those associated with the pure irradiated product.

From the regulatory perspective current UK statutory instruments permit irradiation of foods, subject to appropriate controls[1], and to explicit labelling requirements[2-3]. The recently agreed EU directive on food irradiation[4] makes provision for permitting irradiation of herbs and spices throughout the EU, subject again to explicit labelling. In this case it is significant to note that labelling is required for any food or food product containing irradiated components, at any concentration; a position which reinforces current UK regulations. Moreover the directive calls for the use of validated or standardised methods to be used where possible for market surveillance and regulatory support.

Against this background both thermoluminescence (TL) and photostimulated luminescence (PSL) methods have emerged as the primary detection methods for pure irradiated herbs, spices and related products. Both have been validated for pure product cases. The TL method has been standardised for these cases[5-7], and the PSL method is undergoing standardisation[8]. However standardised classification criteria do not apply explicitly to dilute mixtures of irradiated and unirradiated materials. The purpose of this study is to examine the way in which standard approaches respond to deliberate blending of irradiated and unirradiated materials under controlled conditions.

Both TL and PSL of herbs and spices originate mainly from minerals present as contaminants[9-13]. The standard TL method involves physical extraction of silicates from the food sample, followed by calibrated measurements of TL, and evaluation. Two TL measurements are taken, first glow (G1) comprising the readout of stored radiation induced luminescence from the sample as prepared; the second glow measurement (G2) representing the response to a fixed 1 kGy radiation dose, thus measuring sample sensitivity. Irradiated samples are identified on the basis of a glow ratio (G1/G2) evaluated over a stated temperature interval, coupled with the presence of a G1 glow peak in the 150-250°C region. Quality checks are made to ensure that concordant results are obtained from duplicates, and that each extract has adequate TL sensitivity (in G2) to evaluate the G1/G2 ratio. Thus the TL method involves preparation of a polymineral silicate extract, and evaluation relative to the response of the complete mineral suite to a radiation sensitivity check.

The development of photostimulated luminescence techniques (PSL) for detecting irradiated foods[13-17], was aimed at resolving some of the practical limitations of silicate TL methods. Stored energy from ionising radiation is directly stimulated using pulsed IR sources, and Anti-Stokes luminescence recorded in the UV-VIS band using digital lock-in techniques. Samples can be analysed in a simple screening mode, with limited sample preparation, or using a calibrated method. PSL screening can detect more than 90% of irradiated herb and spice samples using rapid intensity measurements, with a small overlap between high sensitivity unirradiated samples and low sensitivity irradiated samples[13]. Irradiating samples to a known dose and re-reading the PSL signals (CalPSL) allows the sensitivity of the sample to be estimated, resolving the overlap from samples of pure irradiated or unirradiated materials.

Both TL and PSL methods have been through blind intercomparison studies [17], including a series of recent MAFF supported trials[18-21] for a range of food types, with excellent results. They were also used extensively in the 1996 MAFF surveillance exercise[22], succeeding in identifying all blind control samples, and a number of undeclared irradiated spices and spice mixtures.

The presence of dilute irradiated material within a mainly unirradiated matrix has a number of potential effects on the results from standard TL and PSL procedures. It may lead to heterogeneous results - with high coefficients of variation in TL glow ratios, and variable PSL intensities from replicate samples. The magnitude of TL glow ratios from irradiated samples will in general diminish - to an extent which reflects the relative TL sensitivities of irradiated and unirradiated phases. TL glow shapes on G1 may show evidence of low temperature peaks (in the 150-250°C region), but their presence may also be masked by the higher temperature residual geological signals (300-400°C) associated with unirradiated phases. PSL screening interestingly may still respond to many cases of blending, but again the relationship between initial and calibrated PSL response will generally be disturbed by blended products. Thus standard criteria for identification of irradiated products may not be satisfied by blended mixtures. In extreme cases such material may be unidentified; in other cases evidence will be available to indicate that a sample may contain irradiated material.

In the MAFF surveillance study, in addition to those samples which could be reported positively based on validated criteria, several other examples were present in PSL and TL data sets which were consistent with the presence of irradiated material. These could not be classified as irradiated under the study protocol. In wider application experience SURRC has examined more than 2000 samples from commercial sources using PSL, and has conducted some 800 standard TL determinations on commercial material. More than 80 irradiated samples have been detected. A similar or greater number of cases has however been identified which indicate the presence of irradiated material in commercial products, yet which fail to satisfy the criteria for pure irradiated products. This problem was discussed in 1994[13] since when a number of EU TL laboratories have confirmed the incidence of blended materials showing similar characteristics. As noted above, TL classification criteria are based on both glow ratio thresholds and glow shape indicators. In many of the blended cases the glow ratio threshold is not satisfied and the glow shape has many individual elements.

Previous work has shown that, for all products, luminescence sensitivities range over five orders of magnitude. Within a single product the range can span over two to three orders.

The TL glow characteristics are very similar for silicate extracts regardless of the product. With blended products the problem is one of detecting the response of an irradiated component in a dilute mixture containing several different sensitivities from irradiated and unirradiated components. Whereas there are cases with dominant luminescence sensitivities associated with minor irradiated phases, the converse situation will occur in which case the irradiated phase would be undetected.

The aim of this study is to explore the detection rates of standard TL and PSL methods in blended mixtures containing irradiated material at a range of different concentrations and relative luminescence sensitivities. Concentrations of 10%,1% and 0.1% were selected for investigation. It was decided to group luminescence sensitivities into three bands (low, medium and high) and to explore all 9 combinations of the sensitivity of irradiated components ("spike") and unirradiated matrix at each of these concentrations. Six products were selected : three herbs and three spices. Thus for each product a total of 27 blending cases was considered; across the study a total of 162 blended samples were prepared.

Section 2 of the report gives details of the study design including definition of the sensitivity bands for PSL and TL; section 3 describes the selection and amalgamation of retained samples of herbs and spices for use in the study, together with details of irradiation and preparation of the blended samples. Section 4 presents the results of PSL screening measurements on these samples, while section 5 presents the results of standard TL analysis. The results are discussed in section 6, conclusions drawn about the implications for detection of commercial samples, and suggestions for future research to address the underlying issue are considered briefly.

2. Study design and definition of sensitivity bands

The study has been designed with the objective of examining the influence of luminescence sensitivity and concentration of irradiated components on the results of PSL and TL analyses conducted using standard procedures.

Whereas the qualitative effects of blending can be anticipated, and indeed have been observed under commercial analytical conditions (dilution of glow ratios and glow shape indicators in TL analysis, reduction in PSL screening intensities and ambiguous results from calibrated PSL plots) the purpose of this study is to examine systematic effects of blending under controlled conditions. This involves preparing well characterised mixtures of irradiated and unirradiated samples under controlled conditions in the laboratory, and subjecting them to standard analyses. At this stage single ingredient mixtures were prepared, although there is no reason to expect that the results from mixtures of different ingredients would be markedly different.

Since luminescence sensitivity varies widely within individual products, it is to be expected that the outcome of luminescence analysis will depend on both the concentration of the irradiated component, and the relative sensitivities of both the bulk matrix and the irradiated "spike". Therefore the study examined different combinations of concentration and sensitivity of both parts.

For this study, concentration levels of 10%, 1% and 0.1% of irradiated material were selected. To provide a practical design for a short study it was decided to define three sensitivity cases (high, medium and low) for both the matrix (unirradiated) and spike (irradiated), on the basis of calibrated PSL response. Thus for each product a total of 27 irradiated blends were produced. Six products were planned : three herbs and three spices, making a total of 162 samples.

Samples were prepared from mixtures of retained samples from earlier analyses. In selecting material for preparation of the blends, work was needed to establish the expected sensitivities, to examine the relationship between PSL and TL sensitivities for available materials, and to ensure, so far as possible, that material selected for blending had not been previously irradiated, and was well mixed.

The approach to data selection, and definition of sensitivity bands are discussed in the following sections.

2.1.1 SURRC Database and retained samples

A well indexed recording system has been maintained since 1986 when research in this area began, parts of which have been recently transferred to an ACCESS database. We have over 3000 data sets and retained samples, representing authentic unirradiated and irradiated samples plus suspected blends. From the period between late 1993 and 1997 all samples undergoing routine luminescence analysis were subjected to screening and calibrated PSL data, resulting in more than 2000 complete PSL data sets from a wide variety of herbs and spices. More than 800 routine TL analyses have been performed over the whole period, of which a significant subset have accompanying PSL data. Much of these data were available

through an Access database (under development for internal purposes at SURRC), at the onset of the study, and therefore were readily available to define PSL sensitivities for herbs and spices, and to assist with selection of retained samples to prepare the materials for this study.

Retained samples include excess material submitted by external organisations for irradiation testing, samples purchased for PSL research and instrument kits, samples purchased for MAFF funded research and interlaboratory trial samples. The size of retained samples is variable - in some cases there are only 10-50g, where as in other cases there are greater than 500g. All samples have a unique laboratory code, and can be cross-correlated with measured data. The majority of retained samples are considered to be unirradiated on the basis of their credentials and their luminescence results. Others have been identified as irradiated on the basis of their results, and yet others have been classified as potentially containing irradiated materials. For the purpose of sensitivity definition the irradiation status of the sample is unimportant; however for possible inclusion into the materials used for the study only samples classified as unirradiated were considered.

2.1.2 Selection of data for sensitivity analysis

A subset of data from the database was used for sensitivity analysis. The decision to use PSL sensitivity as a primary selection guide for choosing retained samples to prepare blends was based on (i) the availability of a greater number of samples with PSL data than with TL data, and (ii) the ease with which further sensitivity checks could be made during sample handling. The database contains information on more than 29 varieties of herbs, and more than 34 types of individual spices, plus many other product categories including seasonings, vegetables, fruits and shellfish. Two data sets were extracted. Calibrated PSL results were extracted from 957 analysis of herbs and spices (251 herbs, 706 spices) covering the majority of the product codes in these categories. This is referred to as data set "a" below. A second data set drawing together the subset of "a" from which TL data were also available was formed. This contains 215 samples, of which 38 are herbs, and 176 are spices. This is denoted as set "b".

2.1.3 PSL Sensitivity distributions

Sensitivity distributions have been examined from both sets "a" and "b". In both cases the calibrated PSL counts, ie the total photon counts recorded in 60 second measurements in the SURRC PSL system, following irradiation with a 1 kGy gamma dose, are used to define sensitivity. In all cases two aliquots were measured; in some cases up to 6 measurements may have been made. Average calibrated PSL counts were evaluated from each case and used to form a series of histograms, and cumulative frequency diagrams. The range of PSL sensitivities covers up to 5 order of magnitude; however the majority of observations from herbs and spices fall within the range from 10^3-10^6 photon counts. It was decided to examine the 33 and 67 percentile sensitivities - as a general guide to forming sensitivity bands with equal populations from within available data.

Figure 2.1 shows percentage cumulative frequency distributions for herbs and spices from both sets "a" and "b", together with the percentile limits referred to above.

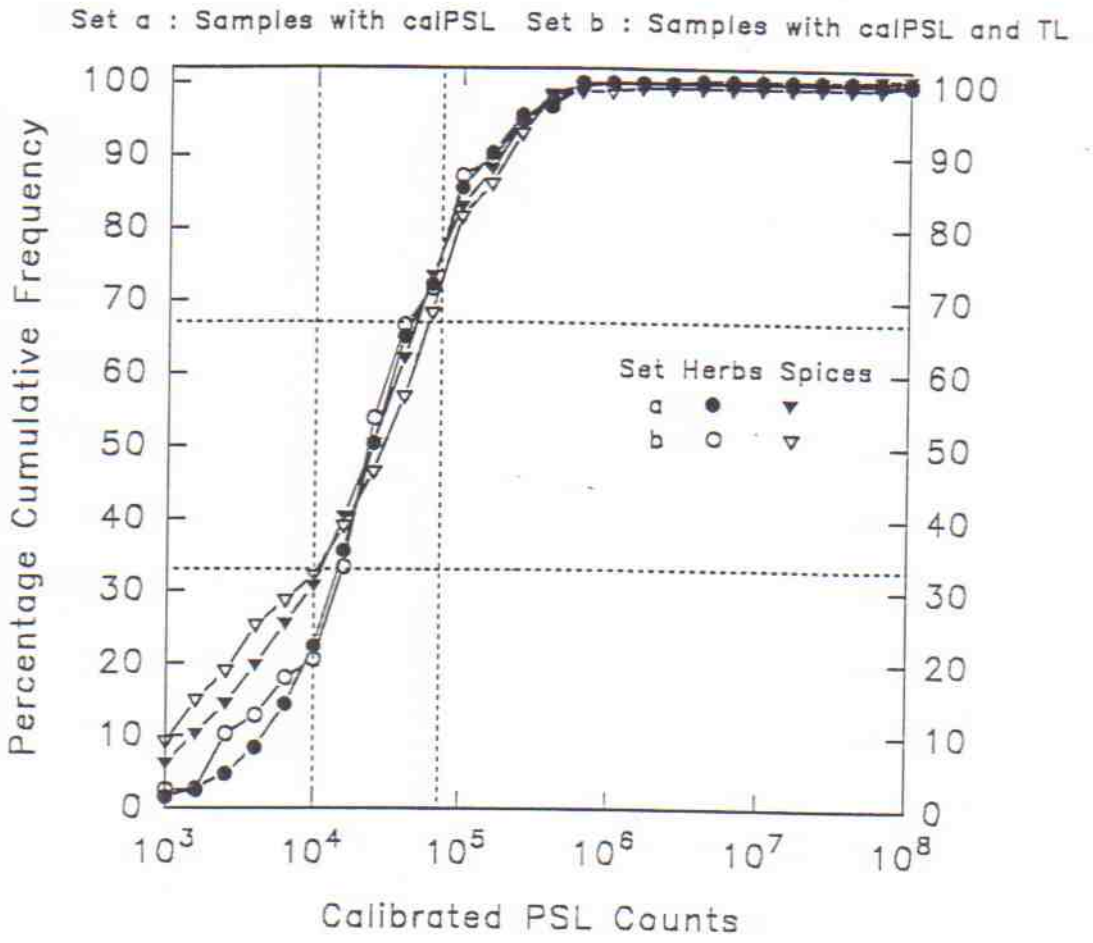


Figure 2.1 PSL sensitivity distributions for herbs and spices. Average PSL counts in 60 second measurements using SURRC PSL equipment following irradiation of samples with a 1 kGy gamma dose. Set a comprises 957 samples of herbs and spices. Set b comprises 215 samples for which TL sensitivity data were also available.

It is apparent that the 33 percentile boundary is approximately 10^4 counts, while the upper boundary occurs between $5x10^4$ and 10^5 counts. At these percentile limits the differences between herbs and spices, and between the smaller and larger data sets are not particularly marked. It is also apparent that there are some differences between herbs and spices at the extremes of the distributions - and in particular at the low sensitivity end - where there are greater numbers of spices than would be expected on the basis of normal statistics. This is probably a reflection of the combined effects of the greater number of spice product types, and perhaps also of the greater extent to which spices are pre-processed (eg cleaned, steamed, peeled etc) to form the products.

The data can be used to define low sensitivity - for the purpose of this study, as corresponding to calibrated PSL response below approximately 10^4; medium sensitivity between 10^4 and $5x10^4$ counts, and high sensitivity $> 5 \times 10^4$.

2.1.4 TL Sensitivity distributions

The sensitivity to TL is defined by the response of samples to a 1 kGy radiation dose administered prior to the second glow (G2) TL measurement. In routine analyses this is used both to check sample sensitivity relative to detection limits, and also to form glow ratios

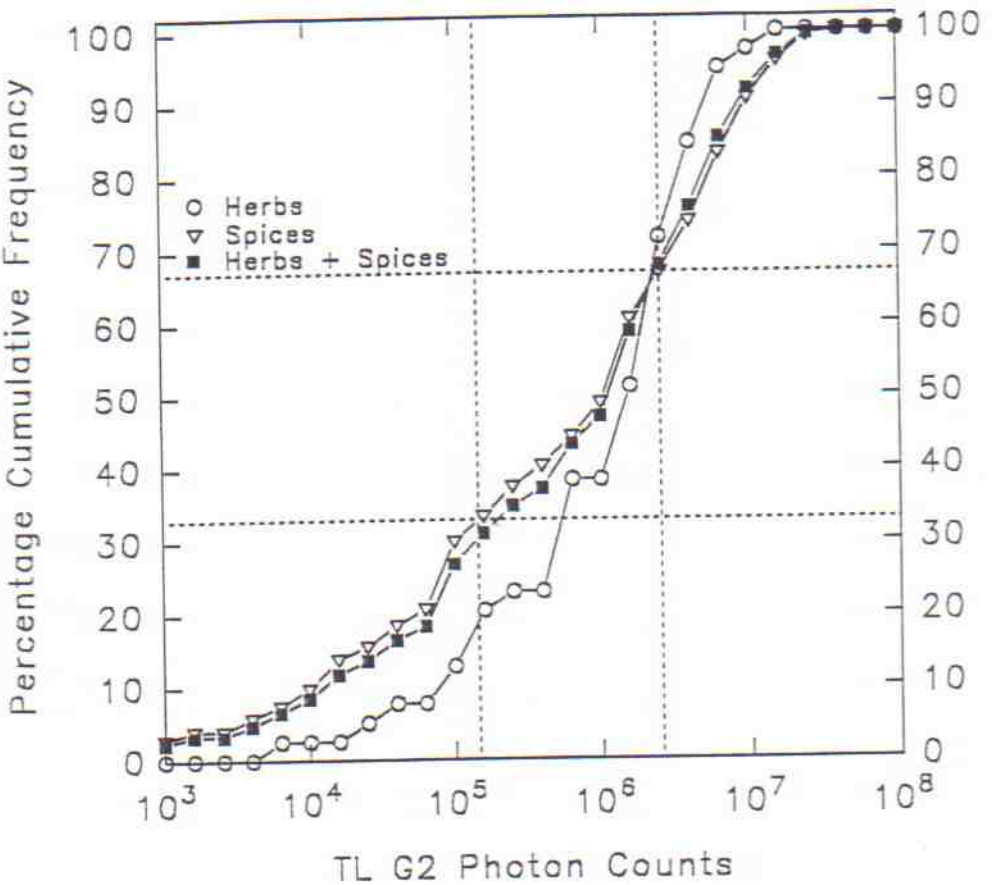


Figure 2.2 TL sensitivity distributions from set b samples. Averaged Glow 2 photon counts from paired aliquots, evaluated from 220-240°C.

relative to the initial TL signal to determine the irradiation status. The value of the second glow TL response is a measure both of the mineral yield from an individual sample, and of the TL sensitivity per unit mass of the minerals from each sample. Figure 2.2 shows the distribution of sensitivities from set "b" samples. Again the range of sensitivities is marked; in this case covering 4 order of magnitude from these samples. As with the PSL data it is notable that the results from herbs show a more restricted distribution; whereas spices - which are of course drawn from a broader set of product types, and may be subject to additional processing, show greater relative populations in both tails of the distributions.

Once again the percentile demarcations of lowest and highest thirds of the population are indicated on the figure. While recognising that the results - particularly for spices - may be

sensitive to product type, and to the rather smaller set of samples used here, compared with PSL, it is possible to define approximate limits for "low", "medium", and "high" sensitivity bands for this study. Thus low TL sensitivity samples may be considered as falling below approximately 200000 counts, high sensitivity greater than 2000000 counts, and medium sensitivity between these limits.

2.1.5 PSL and TL joint sensitivity distributions

Having examined the individual sensitivity distributions for both PSL and TL, and defined working boundaries for low, medium and high sensitivities, it is of interest to examine the extent to which PSL and TL criteria lead to the same classification. It has been stated above that PSL sensitivity will be used for sample selection, and therefore this result will help with the interpretation of any sensitivity related differences revealed between PSL and TL performance from the analyses of blends. Figure 2.3 shows the relationship between TL and PSL sensitivity for set b, together with guidelines corresponding to the 33 and 67 percentile sensitivities defined above.

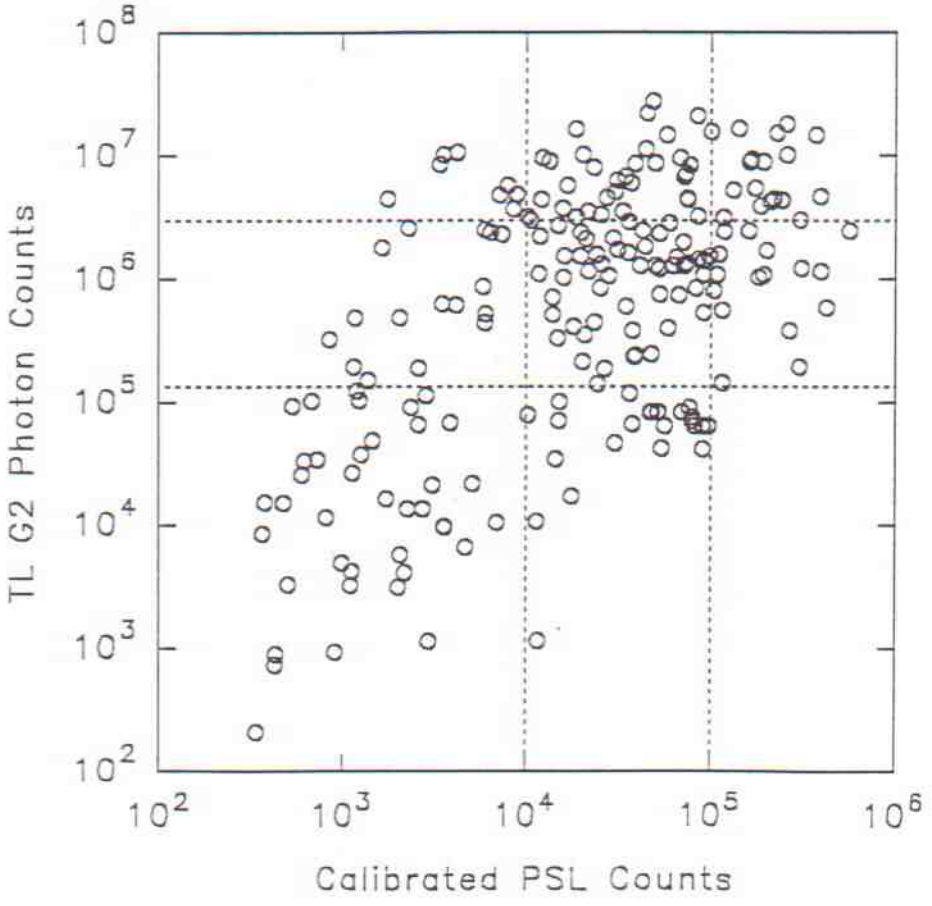


Figure 2.3 The joint TL and PSL sensitivity distribution for set b

There is a correlation between PSL and TL sensitivity, but there is also a considerable amount of scatter about this underlying relationship. Once again mean results from paired analyses are used here. The main reasons for the additional scatter are related to the subsampling statistics of both TL and PSL methods, and to the different manner in which samples are presented for analysis. In TL analysis the minerals are physically extracted and concentrated - usually recovering 10^{-5}-10^{-3} g quantities from samples of 5-10 g. Subsampling statistics for such minor components, distributed heterogeneously, will result in high coefficients of variation in TL sensitivity from sample to sample. Similarly with PSL the measurements are made on surfaces within a 50mm diameter petri dish; the low and variable levels of mineral contaminants resulting in 30-50% coefficients of variation in PSL intensity for individual measurements.

These factors probably explain most of the scatter. It should also be noted however that the mineral suites recorded by TL and PSL may also differ slightly. The routine PSL instrument uses IR stimulation - which accesses feldspars, clay minerals, calcite and soluble salts (eg NaCl), whereas carbonates and soluble salts will not be present in TL signals under standard conditions. Moreover for "thick" source PSL measurements, there will be reflective contributions to the measured signals whose magnitude is sensitive to sample colour.

Notwithstanding the scatter in figure 2.3 it is notable that the majority of observations do correspond to the same sensitivity band by TL as by PSL. There are very few high sensitivity examples by one method, which fall into the low sensitivity band by the other. Similarly those which differ by one sensitivity band (eg boundary cases) are in the minority.

2.1.6 Summary

In summary, PSL and TL sensitivities were examined for two data sets derived from earlier analyses conducted at SURRC. Cumulative frequency distributions were used to define sensitivity levels for PSL and TL based on equal occurrences within the data sets. While differences between herbs and spices, and between products can be inferred, the values derived from the analysis at 33 and 67 percentile levels are not particularly sensitive to product type.

On this basis PSL selection criteria of below 10^4 counts for low sensitivity, and above 5 x 10^4 counts for high sensitivity were defined. The correspondence with TL sensitivity has been examined, and causes of variability discussed.

These criteria were then used to select possible retained samples for preparation of blends. It was decided to use three herbs and three spices. A list of retained samples was assembled, classified by calibrated PSL sensitivities, and reviewed to examine the outcome of TL analysis, the quantities of material available and the likelihood of obtained examples of each product in all three sensitivity bands. This work is described in the next section.

3. Selection and Preparation of materials

Pure products were to be selected; three examples of herb and spice products with all three sensitivity bands (ie 18 pure products). A list was assembled of retained samples, using calibrated PSL sensitivities. Retained samples include excess material submitted by external organisations, samples purchased for PSL research and instrument kits, and interlaboratory trial samples. The size of retained samples is very variable. For the purpose of this project, 500g was the minimum amount required to complete the various analyses. From the list we were able to sift through selecting various products with all three sensitivity bands. For each product selected, the individual TL glow curves was examined carefully for the presence of any minor irradiated material. For those products selected, the amount of retained sample was examined. It became very obvious that amounts of individual retained samples were inadequate, thus it was not possible to obtain the full suite of pure products from single samples.

Two choices were available; one was to purchase from retailers pure products and the other was to bulk products of similar sensitivities. Purchasing products from retailers would result in purchasing many samples and products, testing the sensitivities of each sample using calPSL. A lengthy process and the possibility that would not resolve the problem of obtaining six pure products and their three sensitivity bands. The decision was made to bulk retained samples of similar calPSL sensitivity for each product and homogenise.

From the calPSL sensitivities described in the above section, some difference between herbs and spices was observed, particularly at the low sensitivity end where there are large numbers of spices. A good selection of spice samples was obtained from the assembled list and from this we were able to reduce the choice to three spice samples; paprika, ginger and cinnamon. Their TL data was examined again to ensure that the materials being used to bulk for the final product had not been irradiated.

The choice of herb samples was limited, due to the large number of unirradiated herb samples with naturally high sensitivities. Implementation of the generalised low sensitivity threshold was impractical. One herb sample was selected using the general criteria. To enable further herb samples to be chosen, the lower sensitivity threshold was increased to 20000 counts (this did not affect medium and high sensitivity). From the sample list we were able finally to select the herb samples; basil, oregano and sage. Again the products and their three sensitivities (low, medium and high) were selected on the basis of their calPSL response. The TL data for each sample was again carefully examined for the possibility of a minor irradiated component prior to bulking several retained samples with similar calPSL sensitivity.

This section discusses the matrix and spike materials, the mixing method, preparation of the blended products and their screening PSL results are discussed below.

3.1.1 Preparation of pure products and their irradiations

All the selected samples were bulked from pure products with similar PSL sensitivities, to provide approximately 500g total weight, for each of the three sensitivities (low, medium and high). The samples were homogenised using a hand blender. The final six pure products and their average calPSL for each sensitivity band are shown in Table 3.1.

	Sensitivities					
Sample	**Low**	**PSL**	**Medium**	**PSL**	**High**	**PSL**
Paprika	SP2554	7911	SP1346	15672	SP1413	137449
	SP2555	6382	SP1352	10961	SP1544	90967
	SP1899	6539	SP1353	17910	SP1547	79340
	SP1743	325	SP1349	17107	SP1701	117003
			SP1457	36808	SP2685	79392
			SP1454	20465	SP1651	76073
			SP1481	49858	SP1312	77621
			SP1414	19984	SP1606	63813
	Ave =	**5289**	**Ave =**	**23596**	**Ave =**	**90210**
Ginger	SP2043	2380	SP2169	47541	SP2568	134922
	SP2298	4860	SP2194	53572		
	SP2427	4904	SP2323	44307		
	SP2663	4570	SP2343	28379		
			SP2404	53865		
	Ave =	**4179**	**Ave =**	**45533**	**Ave =**	**134922**
Cinnamon	SP2565	4974	SP1005	10956	SP831	38580
				16088	SP1135	24391
				15000	SP1373	50677
				14740	SP1452	31917
	Ave =	**4974**	**Ave =**	**14196**	**Ave =**	**36391**
Sage	SP2141	23984	SP1014	33531	SP1782	101904
	SP1219	15163	SP2586	24669	SP795	191130
	SP2327	10611			SP1830	124344
	SP1927	18971				
	SP2071	18090				
	Ave =	**17364**	**Ave =**	**29100**	**Ave =**	**139126**
Basil	SP1998	5118	SP1740	12128	SP2578	15205
	SP2002	5154	SP2624	15457		13935
	SP2114	5886	SP1564	12666		
	SP2175	8514	SP1221	12624		
	SP1359	8779	SP2126	11910		
	Ave =	**6690**	**Ave =**	**12957**	**Ave =**	**14570**
Oregano	SP2387	13124	SP1892	55878	SP1012	530016
	SP2385	28710	SP1379	84750	SP2583	123159
	SP2123	2480	SP2796	110530		
	SP2320	7790				
	Ave =	**13026**	**Ave =**	**83719**	**Ave =**	**588326**

Table 3.1 The average calPSL results for the bulked unirradiated products (i.e. the matrices) - samples have had a 1 kGy irradiation dose

Each product was mixed thoroughly using a hand blender and divided into three equally weighed aliquots. Two aliquots for each product's sensitivity band were retained (unirradiated) and the third aliquot (spike) was packed and sent to Isotron for irradiation. The samples received a maximum dose of 10.8 kGy.

Screening PSL results for the 18 unirradiated products are presented in Table 3.2. Note that the higher sensitivity products show a greater incidence of intermediate screening results, in keeping with expectations, most probably as a consequence of their residual geological signals.

PSL Sensitivities

Spike	Low	Medium	High
Paprika	346 353 **Ave= 350**	799 801 **Ave= 800**	1108 1892 **Ave= 1500**
Ginger	388 364 **Ave= 376**	697 735 **Ave= 716**	814 838 **Ave= 826**
Cinnamon	328 318 **Ave= 323**	667 683 **Ave= 675**	792 798 **Ave= 795**
Sage	888 892 **Ave= 890**	890 1228 **Ave= 1059**	1346 1824 **Ave= 1585**
Basil	674 649 **Ave= 648**	871 841 **Ave= 856**	867 943 **Ave= 905**
Oregano	414 426 **Ave= 420**	833 847 **Ave= 840**	888 868 **Ave= 878**

Table 3.2 Screening PSL results for bulked unirradiated products (i.e. the matrices)

The "spike" samples were characterised, on their return from Isotron, using screening PSL to ensure that their response to the irradiation dose was similar to the expected sensitivity bands selected using previous individual calPSL results. The screening PSL results are shown in Table 3.3 for each product. Note that the sensitivities to irradiation is greater for the medium and high sensitivity products, again in keeping with expectations. Also note that the low sensitivity products have higher PSL yields than expected.

PSL Sensitivities

Spike	Low	Medium	High
Paprika	85041 78859 **Ave=81950**	124778 108544 **Ave=116661**	183909 202319 **Ave=193114**
Ginger	17271 22402 **Ave=19837**	22496 18845 **Ave=20671**	192395 212183 **Ave=202289**
Cinnamon	13793 15245 **Ave=14519**	15904 20510 **Ave=18207**	57995 100446 **Ave=79221**
Sage	70300 70267 **Ave=70284**	197987 137665 **Ave=167826**	294874 316515 **Ave=305695**
Basil	37679 37462 **Ave=37571**	46983 48580 **Ave=47782**	60018 75043 **Ave=67531**
Oregano	247385 272225 **Ave=259805**	449335 630482 **Ave=539908**	835241 1003838 **Ave=919540**

Table 3.3 Screening PSL results for bulked products (i.e. the spikes) irradiated to 10 kGy

3.2 Preparation of blends

Blended mixtures containing irradiated material at a range of different concentrations and relative luminescence sensitivities were prepared using concentrations of 10%,1% and 0.1%. The luminescence sensitivities were grouped into three bands (low, medium and high) and all 9 combinations of the sensitivity of irradiated components ("spike") and unirradiated matrix at each of these concentrations were prepared using the six selected products. Thus for each product a total of 27 blending cases were prepared and across the study a total of 162 blended samples.

3.2.1 Comparison of mixing methods

In this study 10%, 1% and 0.1% concentrations of irradiated material had been selected. The materials were to be mixed under controlled conditions, using PSL measurements to assist with quality control measurements. Preparation of blended mixtures was achieved by adding a known weight of irradiated material (spike) to a known weight of unirradiated material (matrix). A number of different food blenders

were tested to mix the irradiated and unirradiated portions together. This section discusses the choice of blender and optimisation of mixing times, preparation, sample coding and identification of the blends.

An experiment designed to establish which food mixer and tool attachment would produce the best mixing, was carried out using 50 g Paprika (unirradiated) + 0.5 g Red Bell pepper (irradiated). PSL signals were measured over set mixing times (10 secs, 30 secs, 1 min and 5 min) for the mixers and tool attachments. The irradiated sample was added to the unirradiated sample and mixed over pre-set time intervals. At the end of each mixing time period, six aliquots were randomly removed and placed into petri-dishes for PSL measurements, following the standard procedure, where an initial PSL signal is compared with two thresholds. For herbs and spices the threshold settings of T1 (lower threshold) 700 counts and T2 (higher threshold) 4000 counts and a cycle time of 60 seconds were used.

Mixer type and tool		**Mixing times (Mean value + std error)**				**Mean levels**
		10s	30s	60s	300s	
Braun Multimix	Balloon whisk	306 ± 235 77%CV	443 ± 378 85%CV	199 ± 103 52%CV	351 ± 232 66%CV	325± 88
Braun Multimix	Chopping tool	232 ± 244 105%CV	201 ± 120 60%CV	295 ± 169 57%CV	173 ± 127 73%CV	225 ±45
Braun Quattro	Cake beater	655 ± 655 100%CV	267 ± 192 71%CV	191 ± 109 57%CV	108 ± 53 49%CV	305 ±210
Braun Quattro	Dough hook	170 ± 182 107%CV	165 ± 202 122%CV	289 ± 262 91%CV	246 ± 241 98%CV	217 ± 52
Background (271 ± 27) already subtracted from results above						268 ± 48

Table 3.4 PSL Results for various mixers, attachments and times.

The samples were then returned to the mixture and the mixing continued for the next mixing time. The results (Table 3.4) show that the Braun Quattro mixer with the cake beater attachment gave slightly better mixing results than the other blender and attachments. The mixing time between 60 seconds to five minutes does not seem to radically change the %CV. It was therefore decided to choose a mixing time of two minutes for the blending experiment with the six products in their various concentrations, matrices and spikes.

3.2.2 Preparation and identification of blend

All the preparation was carried out under safelights. Table 3.5 below, shows the codes used to identify each product. Each product was prepared by working from the lowest concentration through to the higher concentration; using high to low matrix and mixing with the low through to the high spike, to avoid any possibility of contamination.

Sample	Sample Code
Paprika	P
Ginger	G
Cinnamon	C
Sage	S
Basil	B
Oregano	O

Table 3.5 Codes allocated to each sample

Table 3.6 shows the order in which the blended samples were prepared, to minimise the possibility of cross contamination. As in the mixing experiment, the samples were prepared following exactly the same mixing procedure. To a weighed portion of unirradiated sample, a weighed portion of irradiated spike was added and then mixed with the Braun cake beater for two minutes. PSL measurements were carried out on two aliquots, randomly removed from the mixture. The results are described in the following section.

Concentration: 10% Spike

Matrix	Low	Medium	High
Low	Sample Code 9A/B	Sample Code 18A/B	Sample Code 27A/B
Medium	Sample Code 8A/B	Sample Code 17A/B	Sample Code 26A/B
High	Sample Code 7A/B	Sample Code 16A/B	Sample Code 25A/B

Concentration: 1% Spike

Matrix	Low	Medium	High
Low	Sample Code 6A/B	Sample Code 15A/B	Sample Code 24A/B
Medium	Sample Code 5A/B	Sample Code 14A/B	Sample Code 23A/B
High	Sample Code 4A/B	Sample Code 13A/B	Sample Code 22A/B

Concentration: 0.1% Spike

Matrix	Low	Medium	High
Low	Sample Code 3A/B	Sample Code 12A/B	Sample Code 21A/B
Medium	Sample Code 2A/B	Sample Code 11A/B	Sample Code 20A/B
High	Sample Code 1A/B	Sample Code 10A/B	Sample Code 19A/B

Table 3.6 The order of preparation for each of the blend

4. PSL analysis

PSL provides an extremely fast procedure for testing for the presence of irradiated foods. The PSL signal is dependent upon the total absorbed dose. Using PSL it is possible to excite anti-stokes luminescence from irradiated samples. Unirradiated samples show low signals which are mainly due to the samples natural background.

The problem of blended products has been noticed over a period of several years, since 1992/3. The effect of introducing a minor irradiated component plays a crucial part in whether a sample will be detected or not. For this reason this project was undertaken with the aim of exploring the introduction of an irradiated pure product (spike) at three different concentration levels; 10%, 1% and 0.1% into a range of pure unirradiated product (matrix) using six pure products (three herb and three spice samples).

PSL analysis has been used in the initial set of experiments as a quality check In this section PSL was employed to see the extent to which minor irradiated component can be detected by screening measurements, with respect to matrix and spike sensitivity and concentration levels.

The blended products, prepared as described in the section above, were placed in well labelled bottles and set aside for TL analysis. PSL measurements were carried out on two aliquots, randomly removed from the mixture. The results for screening PSL for each blended product are described in this section.

4.1 Standard screening procedure

The draft European standard method was followed for sample handling, measurement and assessment. The screening procedure involves an initial PSL measurement where the signal is compared with two thresholds. For herbs and spices the threshold settings of T1 (lower threshold) 700 counts and T2 (higher threshold) 4000 counts and a cycle time of 60 seconds were used. The majority of irradiated samples produce strong signals above T2, and signals below T1 suggest that the sample is unirradiated. Samples which produce a signal between these two threshold (intermediate) suggest that further investigation should be carried out by calibration or TL.

Samples were dispensed in duplicate as a thin layer into petri-dishes and presented for measurement. The PSL instrument was set up following standard procedure which involves light and dark count to be measured, analysis of unirradiated and irradiated standards and empty chamber tests. Empty chamber tests were also carried out at regular intervals and after any high reading through out the runs. The screening results were recorded and stored on disc both in summary and individual results. Classification relative to the thresholds are automatically appended to these files.

4.2 Screening intensities for each product

The screening intensities for each product; paprika, ginger, cinnamon, basil, oregano and sage, and at each concentration level and sensitivity cases for both matrix and spike, are shown in Tables 4.7 - 4.12.

These tables show that, as might have been expected, in general the higher concentrations of irradiated material, and the higher sensitivities of irradiated spikes, lend to higher PSL screening results.

At 10% concentration all samples give either intermediate or positive intensities, whereas at 1% or 0.1% concentrations the proportions of negative or intermediate levels increase.

For the products of paprika, oregano and sage, screening PSL results showed similar trends. At 10% concentration positive results were obtained for all sensitivity cases for both matrix and spike. As the concentration level decreased from 1% to 0.1% the number of positive results diminished, intermediate and negative results increased for both matrix and spike sensitivities.

In the cases of cinnamon, ginger and basil at 10% concentration the proportion of intermediate results is very much higher than the proportion of positive results. At the 1% and 0.1% concentrations we have a significantly larger number of intermediate and negative results than those from the other three samples. However, this may only be the result of the random sampling, the probability of having irradiated minerals within the duplicate aliquots, especially at the lower concentrations or the mixing.

Paprika

Concentration: 10% **Spike**

Matrix	Low	Medium	High
Low	24543	7741	17579
	2933	10299	28729
Medium	4737	8424	31862
	4262	8839	13555
High	3937	12376	17882
	4304	5629	13617

Concentration: 1% **Spike**

Matrix	Low	Medium	High
Low	2565	619	1380
	451	568	733
Medium	767	446	2567
	825	1882	2303
High	689	1992	1827
	575	1373	2729

Concentration: 0.1% **Spike**

Matrix	Low	Medium	High
Low	243	281	254
	252	287	352
Medium	929	526	788
	608	569	646
High	438	539	531
	398	818	544

Table 4.7 Screening PSL results for the duplicate aliquots of blended paprika removed from the sample prior to TL analysis.

Ginger

Concentration: 10% **Spike**

Matrix	Low	Medium	High
Low	2323	724	24084
	1495	1493	9821
Medium	1687	36366	25923
	5198	2804	34308
High	4205	3693	50346
	1072	3506	95965

Concentration: 1% **Spike**

Matrix	Low	Medium	High
Low	384	404	23327
	870	25027	19798
Medium	380	9417	6827
	278	23110	5673
High	840	20167	11071
	1168	4274	28953

Concentration: 0.1% **Spike**

Matrix	Low	Medium	High
Low	295	277	651
	277	301	4158
Medium	287	335	294
	304	397	4058
High	534	1084	2097
	704	1381	693

Table 4.8 Screening PSL results for the duplicate aliquots of blended ginger removed from the sample prior to TL analysis.

Cinnamon

Concentration: 10% Spike

Matrix	Low	Medium	High
Low	1440	837	3452
	1341	617	5475
Medium	1377	1372	6412
	1344	891	10217
High	5250	549	7044
	2608	1222	10482

Concentration: 1% Spike

Matrix	Low	Medium	High
Low	844	410	472
	451	192	579
Medium	419	399	484
	730	418	2219
High	543	559	714
	587	691	1677

Concentration: 0.1% Spike

Matrix	Low	Medium	High
Low	487	369	318
	325	341	320
Medium	421	317	265
	434	315	291
High	548	486	501
	532	571	437

Table 4.9 Screening PSL results for the duplicate aliquots of blended cinnamon removed from the sample prior to TL analysis.

Sage

Concentration: 10% Spike

Matrix	Low	Medium	High
Low	7604	8062	11255
	7630	7651	11440
Medium	6050	6507	14194
	8175	9292	13382
High	9200	8940	12095
	3452	3582	14118

Concentration: 1% Spike

Matrix	Low	Medium	High
Low	458	315	1015
	384	370	1185
Medium	1109	484	1345
	2872	525	2381
High	431	425	1041
	564	404	927

Concentration: 0.1% Spike

Matrix	Low	Medium	High
Low	370	352	397
	388	309	409
Medium	409	420	488
	475	574	390
High	359	478	507
	371	414	539

Table 4.10 Screening PSL results for the duplicate aliquots of blended sage removed from the sample prior to TL analysis.

Basil

Concentration: 10% Spike

Matrix	Low	Medium	High
Low	3041	4322	6236
	2424	3037	5240
Medium	3567	4027	7632
	2907	4017	11907
High	2778	11893	2701
	2106	1779	2511

Concentration: 1% Spike

Matrix	Low	Medium	High
Low	457	1024	587
	372	589	726
Medium	2095	846	2785
	1477	823	3199
High	278	510	392
	476	343	544

Concentration: 0.1% Spike

Matrix	Low	Medium	High
Low	361	262	240
	410	371	293
Medium	1056	4612	1317
	1691	1126	1612
High	281	300	278
	286	336	330

Table 4.11 Screening PSL results for the duplicate aliquots of blended basil removed from the sample prior to TL analysis.

Oregano

Concentration: 10% Spike

Matrix	Low	Medium	High
Low	70844	15680	53775
	85051	12425	74239
Medium	75631	17194	70097
	61182	19721	87475
High	90177	32649	59534
	56852	21542	94726

Concentration: 1% Spike

Matrix	Low	Medium	High
Low	5053	2880	6314
	7868	899	5169
Medium	4535	2700	5380
	3805	3302	15133
High	3352	2491	12490
	10195	2658	5861

Concentration: 0.1% Spike

Matrix	Low	Medium	High
Low	692	382	893
	662	744	647
Medium	1947	581	846
	1963	713	862
High	1241	629	959
	838	699	649

Table 4.12 Screening PSL results for the duplicate aliquots of blended oregano removed from the sample prior to TL analysis.

4.3 Screening performance for all products

The screening results for all products at the three concentration levels are summarised in Table 4.13. At 10% concentration for all products and the 3 sensitivity cases for both matrix and spike, using the highest duplicate measurement (a total of 54 results), we observe no negative results, and 69% giving positive results with the remaining 31%, an intermediate result was observed. As we go across the table from low to high spike we do observe that the percentage of positive results increases with a decrease in percentage of intermediate cases. Thus 100% of samples at 10% concentration are detected with either intermediate or positive screening results.

For all products in the 1% concentration, only 20% of the total measurements (highest duplicate) produced a positive result, 48% giving an intermediate signal and 32% giving a negative result. Again, it is notable, that as we move to the high spike the number of positive identifications increase and there is a spread of results giving intermediate and negative signals. Thus at 1% concentration 68% of samples are detected in intermediate or positive.

At 0.1% concentration there are no positive results over all the products, in all three sensitivity cases for both matrix and spike. A higher number of negative results (67%) as recorded, compared with only 33% of samples giving intermediate results. It is interesting to note that the results from high sensitivity matrices are not showing the same residual geological levels here as had been observed with the pure unirradiated products (see Table 3.2, section 3.1). This may be an indication that the additional mixing operation in preparing the blends has released trapped minerals within the unirradiated matrix. However this explanation has not been investigated experimentally at this stage.

These results are presented graphically in Figure 4.4. We observe overall that at 10% concentration, PSL can reliably detect the irradiated component regardless of sensitivity from either the spike or matrix. However at 1% concentration the detection rate in intermediate or positive bands falls to 67%, and at 0.1% concentration it is only 33%.

Of course intermediate screening results are not conclusive demonstration of irradiation, although they are suggestive of it. However from Figure 4.4 it can be seen that at 1% concentrations there is still a response which increases with spike sensitivity, indicating that the signal contribution from the irradiated component is still significant. This is less clear at 0.1% concentration.

Given that the TL analysis is the primary method for attempting to resolve intermediate PSL results, it is of interest to see how the TL method performs with the same samples.

Concentration: 10% Spike

Matrix	Low	Medium	High	Total
Low	3 Positive 3 Intermediate	3 Positive 3 Intermediate	6 Positive	12 Positive 6 Intermediate
Medium	3 Positive 3 Intermediate	4 Positive 2 Intermediate	6 Positive	13 Positive 5 Intermediate
High	3 Positive 3 Intermediate	4 Positive 2 Intermediate	5 Positive 1 Intermediate	12 Positive 6 Intermediate
Total	9 Positive 9 Intermediate	11 Positive 7 Intermediate	17 Positive 1 Intermediate	37 Positive 17 Intermediate

Concentration: 1% Spike

Matrix	Low	Medium	High	Total
Low	1 Positive 3 Intermediate 2 Unirradiated	1 Positive 2 Intermediate 3 Negative	2 Positive 3 Intermediate 1 Negative	4 Positive 8 Intermediate 6 Negative
Medium	5 Intermediate 1 Negative	1 Positive 3 Intermediate 2 Negative	2 Positive 4 Intermediate	3 Positive 12 Intermediate 3 Negative
High	1 Positive 1 Intermediate 4 Negative	1 Positive 2 Intermediate 3 Negative	2 Positive 3 Intermediate 1 Negative	4 Positive 6 Intermediate 8 Negative
Total	2 Positive 9 Intermediate 7 Negative	3 Positive 7 Intermediate 8 Negative	6 Positive 10 Intermediate 2 Negative	11 Positive 26 Intermediate 17 Negative

Concentration: 0.1% Spike

Matrix	Low	Medium	High	Total
Low	6 Negative	1 Intermediate 5 Negative	2 Intermediate 4 Negative	3 Intermediate 15 Negative
Medium	3 Intermediate 3 Negative	2 Intermediate 4 Negative	4 Intermediate 2 Negative	9 Intermediate 9 Negative
High	2 Intermediate 4 Negative	2 Intermediate 4 Negative	2 Intermediate 4 Negative	6 Intermediate 12 Negative
Total	5 Intermediate 13 Negative	5 Intermediate 13 Negative	8 Intermediate 10 Negative	18 Intermediate 36 Negative

Table 4.13 Overall PSL Results for all products using the highest value from duplicate results

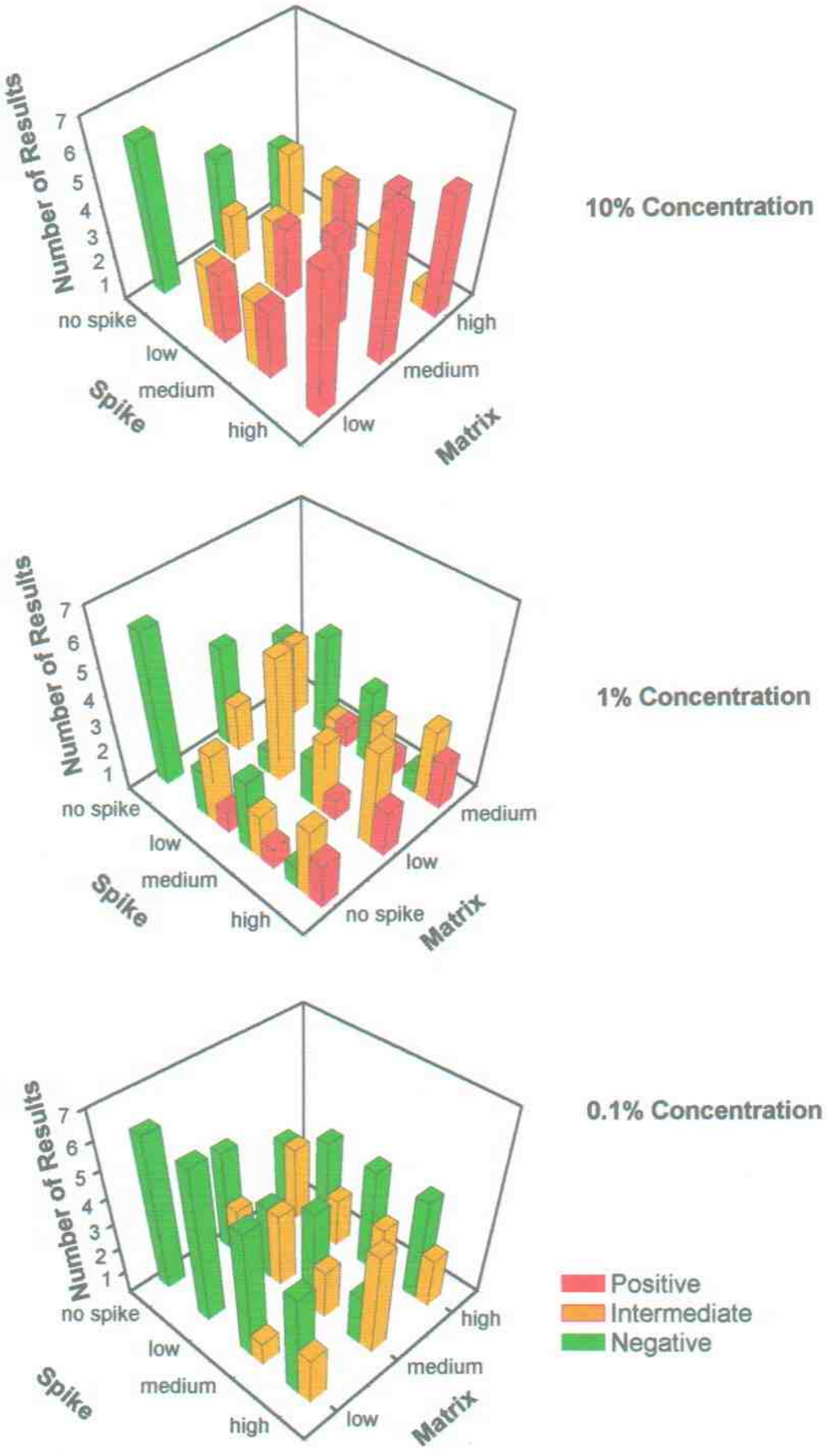


Figure 4.4 PSL screening results for all herb and spice products

5. TL analysis

The TL method has been shown to be a very effective technique for detecting irradiated foods containing silicate material. Validation of the TL method has been achieved through many interlaboratory trials and on a variety of food products. Routine TL analyses are conducted in many countries and have detected numerous unlabelled irradiated foods. These materials are however pure products which have been thoroughly checked for any anomalities. A shortcoming of interlaboratory trials are that they are carried out under controlled conditions using "blind" samples which may not be totally representative of what is really being sold in a commercial market. Results from these trials are evaluated, leading to specific detection criteria for these products.

Herbs, spices and seasonings are frequently blended for many reasons from making seasoning mixtures to specific colour and texture criteria. Individual herbs and spices can comprise of several tonnes of consolidated batches of material from various sources. Blended products, especially those which have a minor irradiated component within an unirradiated matrix, could dramatically affect whether the sample would be classified as irradiated or not, using standard detection criteria.

This section discusses the results, using the standard TL technique and detection criteria, on the six products when an irradiated pure product (spike) is introduced at the three different concentration levels into the pure unirradiated product (matrix).

5.1 Standard TL procedure

The standard TL procedure, EN1788 was followed for the sample preparation, measurement and assessment. Silicate minerals are separated from the product using agitation in water, preconcentration of the minerals, separation of the minerals from organic material using sodium polytungstate and an acid clean up prior to dispensing on stainless steel discs for TL readout. Measurement of first glow (G1) TL from room temperature to 400° C at 5° Cs^{-1} is recorded, then the samples are irradiated prior to recording second glow (TL) TL. Instrumental background measurements are conducted, as are the measurements of process blanks to enable evaluation of the minimum detectable level (MDL).

The identification of an irradiated sample by TL using EN1788 criteria, depends on the glow ratio value (G1/G2) and the shape of G1. The temperature interval for evaluation of the TL glow ratio is in the range of 150° C to 250° C. The absolute temperature scale may be defined by the evaluation of glow curves obtained from lithium fluoride (LiF).

In the original UK validated method (MAFF V27, 1992) it was noted that unirradiated herbs and spices normally had glow ratios G1/G2 < 0.1, whereas irradiated products usually gave G1/G2 > 1, and that the presence of a low temperature peak (between 150 - 250° C) provided an additional indicator of an irradiated product.

The EN 1788 criteria published in 1996 adopted a formal classification scheme whereby samples with G1/G2 > 0.5 were considered irradiated, regardless of G1 peak shape. Samples with 0.1 < G1/G2 < 0.5 accompanied by a peak in the 150 - 250° C region were considered irradiated, and samples with G1/G2 < 0.1 were always classified as negative.

However increasing recognition of the impact of blending in samples with a-typical characteristics has led to the proposal of revised criteria for EN 1788. The 1998 EN1788 criteria are that all samples classified as irradiated must show a peak between 150 and 250° C in G1 curves, and have ratios G1/G2 > 0.1. The existence of samples with G1/G2 < 0.1 and clear peaks is acknowledged for blended samples, but no clear classification guidance for this is given.

Against this back ground it is of interest to examine the samples prepared here against both EN 1788 (1996) and the revised EN1788 (1998) criteria.

5.2 Preparatory work

All the preparation was carried out under safelight conditions. Products were prepared separately working from the lowest concentration through to the higher concentration, using high to low matrix and low spike to high spike, to minimise possible contamination. The procedure for separation of minerals was carried out using the steps detailed in EN1788.

Calibration of the absolute temperature scale of the two SURRC TL readers was carried out using LiF, prior to sample readout. For both readers the position of peak V (=PV) and peak VI were measured on a set of four LiF pellets and the temperature difference (IS) between the two values calculated. The temperature interval recommended by EN1788, is (PV-IS) to PV. Table 5.1 below show the results from the SURRC TL readers. In previous interlaboratory trials both TL readers had given consistent LiF results with peak V close to 250° C. The lower effective temperature obtained from PC1 (220° C) in this study resulted from a change in heater plate in 1998 to one with a thermocouple contact slightly removed from the heater plate base. Thus the thermocouple underestimates the heater plate temperature. This has been observed in analyses of quartz conducted in late 1998, and for experimental reasons it was decided to postpone the thermocouple change until the complete series of quartz analyses and these TL analyses was implemented; to avoid loss of comparability between long term data sets.

LiF Peak V (PV) °C		LiF Peak VI °C	
PC 1	**PC 2**	**PC 1**	**PC 2**
219	264	270	331
219	261	269	333
222	261	272	320
221	258	272	323
Mean value 220 ± 1.50	261 ± 2.45	271 ± 1.50	327 ± 6.23

Table 5..1 LiF Results for SURRC TL readers

It should be noted that the temperature offset between these readers is small compared with the range of values reported between European laboratories in the many interlaboratory trials conducted between 1991 and 1997. Appropriate integration bands were selected for both PC1 and PC2 to correspond to EN 1788 recommendations, and to produce comparable results from both instruments.

5.3 TL Results for each product

TL analysis was carried out on the six products (paprika, ginger, cinnamon, sage, basil and oregano) at the three concentration levels and sensitivity cases. A total of 162 pairs of TL measurements as conducted, along with process blanks. In each case the results were examined in detail, and eight samples were rejected due to their data being associated with specific analytical problems.

Figures 5.1 - 5.3 illustrate for one of the products (Oregano), the first glow (G1) glow curves for 10%, 1% and 0.1% concentrations as a function of matrix and spike sensitivities. A number of features emerge as far as the presence of the low temperature peak is concerned. Looking at the 10% concentration first, the glow curves for low and medium sensitivity matrices are dominated by the signal from the irradiated phase; in all cases peaking at 150 - 200° C. By contrast the high sensitivity

matrix shows an additional glow curve component, peaking at 250 - 300° C; which corresponds to natural or geological residual signal in the silicates. This is most pronounced in the case with the low sensitivity spike; where a double peaked glow curve is observed. However, the low temperature signal from the irradiated spike is clearly detected in all cases at 10% concentration.

At 1% concentration (Figure 5.2) both components are visible in the majority of the glow curves, although it is notable that the high temperature component is dominant in one case from the medium sensitivity matrix and in two cases from the high sensitivity matrix.

At 0.1% concentration (Figure 5.3) the high temperature signal is more prominent still, relative to the low temperature component. In only three cases is the irradiated signal dominant, although it is present - if only as a minor shoulder, in every case.

These curves illustrate the peak shape effects of blending for one product. Tables 5.1 - 5.6 summarise the G1 and G2 intensities, G1/G2 ratios and the status of the low temperature peak for all six products respectively. The following sections summarise this information with respect to EN 1788 (1998) criteria; thereafter the data are considered relative to EN 1788 (1996) criteria for comparative purposes.

Paprika (Table 5.1)

For paprika at 10% concentration case, all TL results satisfied the proposed 1998 European standard criteria; all gave glow ratios greater than 0.1 and a positive peak at the predefined temperature interval. For both matrix and spike sensitivities at this concentration, 100% correct classification that the sample had been irradiated was achieved. Under EN1788 1996 criteria all samples would also be correctly classified, although it is notable that only three samples exceed G1/G2 > 0.5

At 1% concentration case; only one positive result was obtained for the high matrix with high spike. All three matrices (high, medium and low) with medium sensitivity spike, satisfied the classification criteria for an irradiated product. Discordant results were observed for the low matrix high spike blend. The remaining matrix and spike cases glow curves showed either a shoulder or small peak with glow ratios less than 0.1.

From the medium matrix and low sensitivity spike at 0.1% concentration, only one positive result was obtained. For all the remaining matrix and spike sensitivity cases at 0.1% concentration, negative glow ratios were obtained with the glow curves showing either a small shoulder or small peak.

Ginger (Table 5.2)

For ginger at 10% concentration, only the mixes of medium matrix with low spike, high matrix with medium spike, medium and high matrices with high spike would have been detected using the standard criteria for pure products. The remaining cases did show some evidence of an irradiated component, by the presence in the glow curve of a peak. Their glow ratios however did not satisfy the classification criteria.

For all matrices with the high spike at 1% concentration, satisfied both glow ratio and glow curve criteria and would be detected as irradiated. Discordant results were obtained for high matrix with medium spike. For all the matrices with low spike and low and medium matrices with medium spike would be classified as unirradiated using the standard method. The majority of these cases showed no evidence of an irradiated component in the glow curve.

At 0.1% concentration, discordant results (one positive aliquot and one negative aliquot) were obtained for low matrix with low spike, medium matrix with medium spike and high matrix with high spike. All the other samples, using standard classification would have been identified as unirradiated.

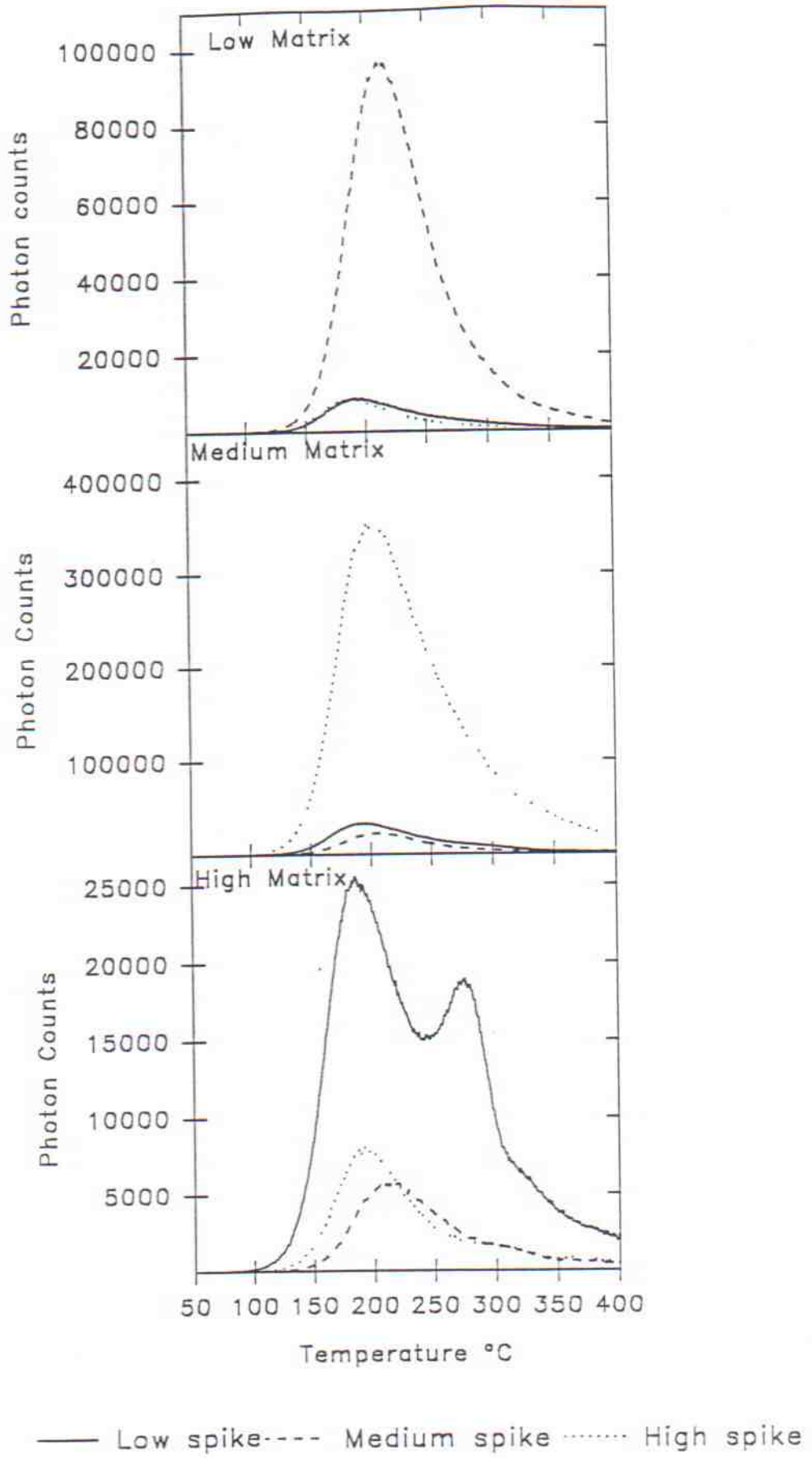


Figure 5.1 TL first glow curves for 10% Oregano

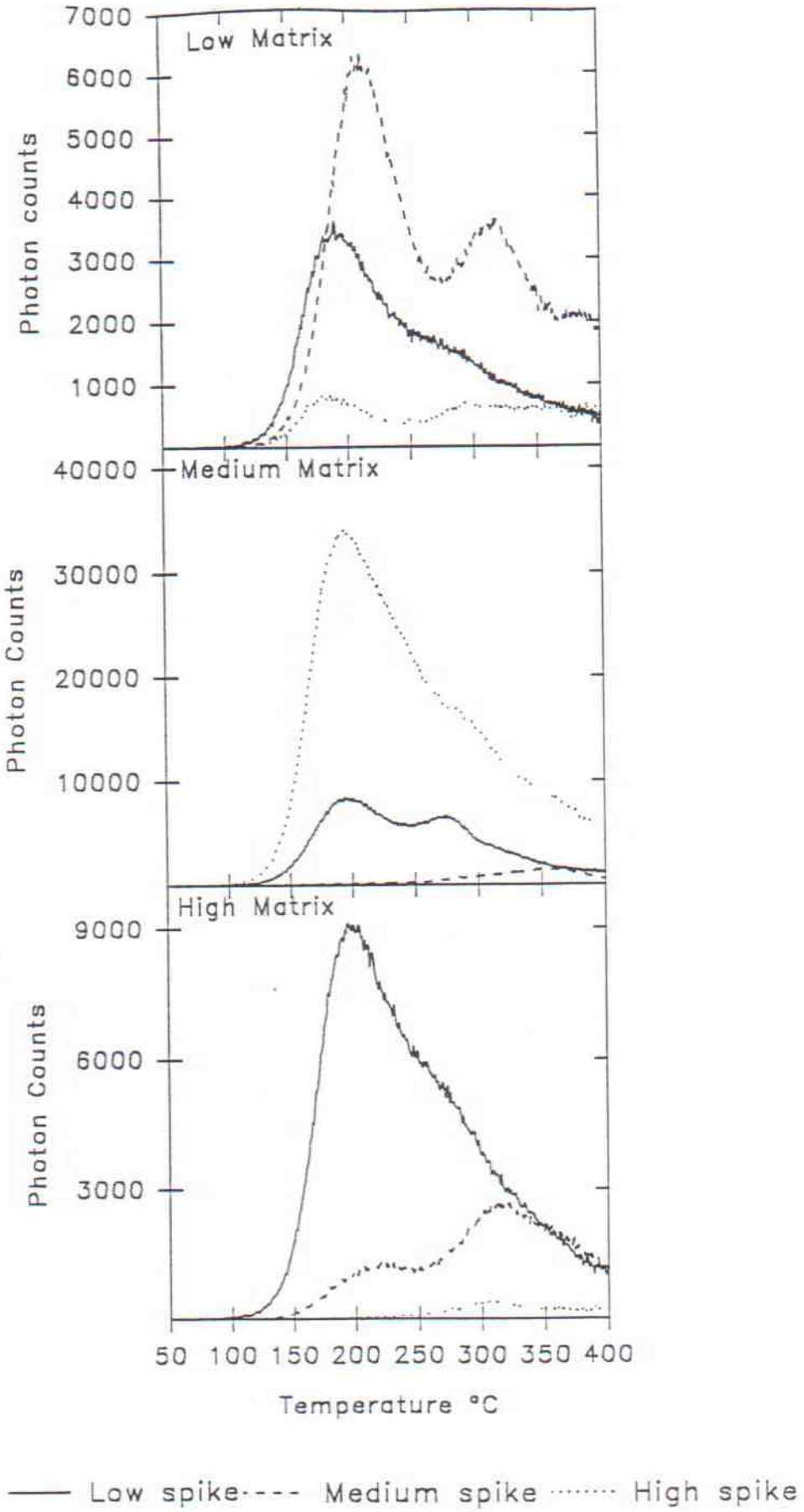


Figure 5.2 TL first glow curves for 1% Oregano

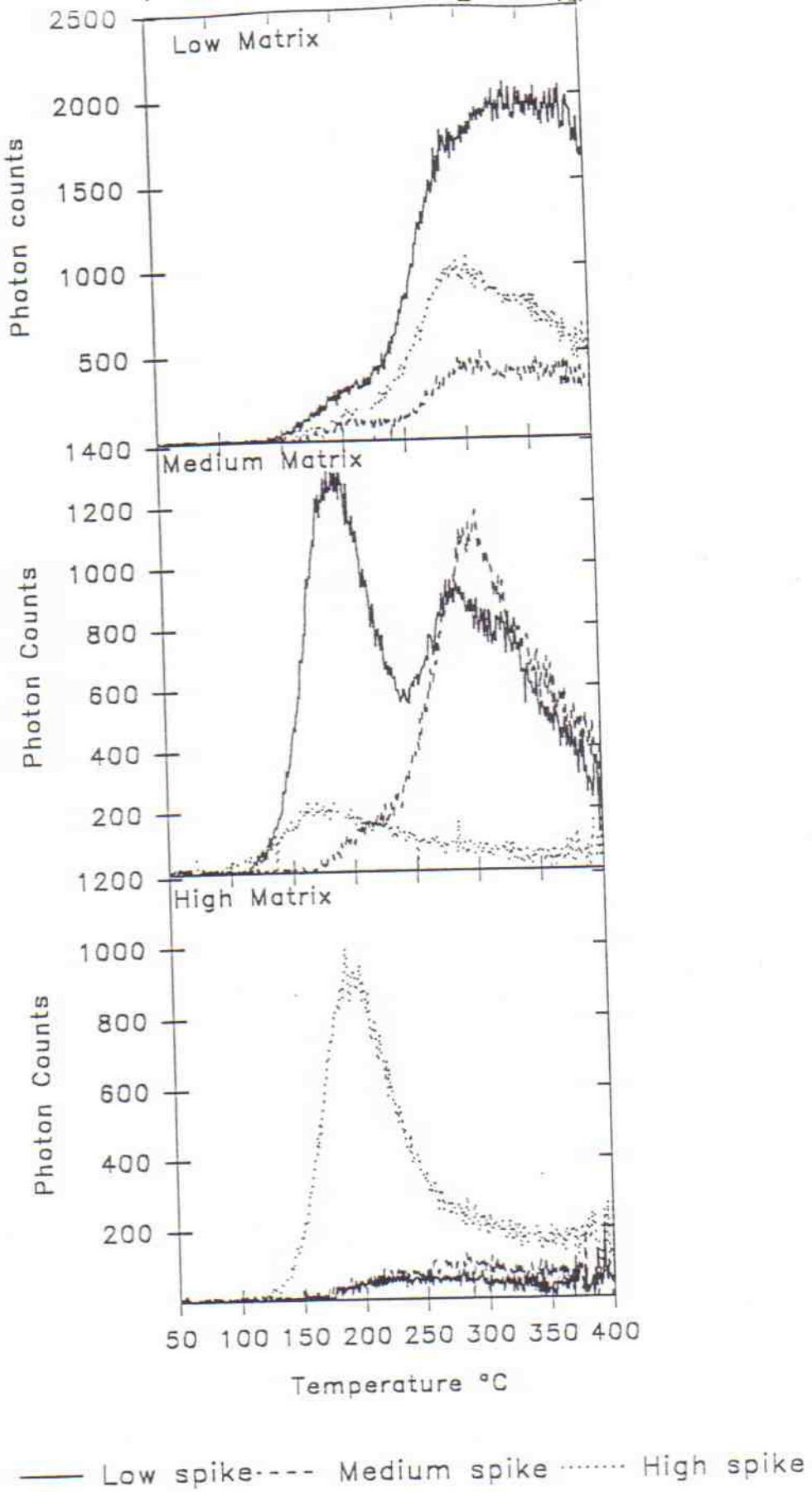


Figure 5.3 TL first glow curves for 0.1% Oregano

Cinnamon (Table 5.3)

The TL results for cinnamon at the 10% concentration for matrix and spike at the three sensitivity cases, were identified correctly as being irradiated from glow ratio and glow shape criteria.

Those samples at the 1% concentration which satisfied the criteria for being irradiated were; low matrix with both medium and high spike, and medium matrix with both low and medium spike. Two samples; high spike with both medium and high sensitivity matrices, gave from duplicate aliquots, one irradiated and one unirradiated result. The TL results from the three remaining mixtures (low matrix with low spike and high matrix with low and medium spikes) gave negative glow ratios and a shoulder on the glow curve.

At the 0.1% concentration, for all matrices with low spike, only two samples from single aliquots, satisfied the standard criteria for an irradiated product. The remainder of these matrices with low spike did show either a peak or shoulder, however, their glow ratios were less than 0.1. In the case with medium spike with all three matrices, all samples would have been classified as unirradiated using standard criteria. For the high spike with all three sensitivity matrices, only two positive glow ratios were observed from single aliquots of low and high matrices. The remainder had negative glow ratios and in all cases the evidence of a shoulder.

Sage (Table 5.4)

For sage at 10% concentration, matrices with low and high spikes satisfied the irradiated identification criteria. Low matrix, medium spike and high matrix, medium spike gave a glow ratio less than 0.1, however, a clear peak was observed in these cases.

At 1% concentration for all matrices and spike sensitivities an irradiated component was observed in the glow curves. However, only one aliquot of low matrix, low spike and medium matrix high spike gave glow ratios greater than 0.1, the remaining samples gave glow ratios below the 0.1 criteria.

At 0.1% concentration, no sample gave glow ratios which would satisfy the standard criteria. For the majority of the samples, some evidence that there may be an irradiated component from a shoulder observed in the glow curve. However, all samples at this concentration would be classified as negative using the standard criteria.

Basil (Table 5.5)

Basil at 10% concentration and all matrix and spike sensitivities, gave TL results, which satisfied the European standard criteria for irradiated products.

In the 1% concentration case, the medium matrix with the three sensitivity spikes satisfied the standard glow ratio and peak maxima criteria and were detected as having been irradiated. The remaining cases gave discordant or negative results. The low spike with matrix gave negative results, with one aliquot showing a slight shoulder. Low and high matrices with high spike, gave negative glow ratios with a small peak.

The high matrix and three spikes and the low matrix with medium spike, at 0.1% concentration, all produced negative glow ratios and no evidence of an irradiated component in the glow curve. For low matrix with low and high spike at this concentration we see evidence of a peak in the glow curve, however, glow ratios are less than 0.1. In the medium matrix with all three spike sensitivities we observe strong evidence of an irradiated component in the glow curve and in all cases but medium with medium (where there is discordance), glow ratios of greater than 0.1 are observed.

Oregano (Table 5.6)

10% oregano with all matrices , low and medium spike were detected. As were the low, medium matrices with low and medium spike. The high matrix with high spike gave a positive peak but glow ratios of less than 0.1.

At 1% concentration, only the medium matrix with high spike would have been identified as irradiated. The low matrix with low and medium spike gave discordant results, and the remaining samples all giving negative glow ratios. However, for all these mixes, there was evidence in the glow curve either by a peak or a shoulder, that an irradiated component was present.

Only one aliquot at 0.1% concentration gave a positive glow ratio with the remaining samples being identified with negative glow ratios. In most of the cases there was some evidence from the glow curves of a shoulder or small peak.

Paprika

Concentration: 10% Spike

Mat	Low				Medium				High			
	G1	G2	G1/G2	P	G1	G2	G1/G2	P	G1	G2	G1/G2	P
Low	596090	2241448	0.3	++	368941	344356	1.1	++	456386	561459	0.8	++
	56702	465358	0.1	+	771104	1783837	0.4	++	511767	1632530	0.3	++
Med	198633	1135966	0.2	+	92991	291005	0.3	++	475477	889874	0.5	++
	103287	773386	0.1	+	139457	1428671	0.1	++	943047	409085	2.3	++
High	135859	459126	0.3	++	7452	71248	0.1	+	191420	587383	0.3	++
	213330	1654528	0.1	++	151523	556070	0.3	++	267908	1368571	0.2	++

Concentration: 1% Spike

Mat	Low				Medium				High			
	G1	G2	G1/G2	P	G1	G2	G1/G2	P	G1	G2	G1/G2	P
Low	107759	6208415	0.020	+	14923	1297172	1.07	+	14008	1068329	0.01	?
	2437	581556	0.004	?	1679	71248	0.43	?	230308	199704	1.15	+
Med	49400	688365	0.070	+	4817	312209	0.32	+	19048	2697270	0.007	+
	2600	618312	0.004	?	9453	1443706	0.10	+	126931	5119213	0.025	+
High	82818	4875915	0.02	+	1422	657151	0.10	+	6050	1031369	0.006	-
	139122	4217153	0.03	+	1743	404097	0.27	+	3339	314086	0.011	-

Concentration: 0.1% Spike

Mat	Low				Medium				High			
	G1	G2	G1/G2	P	G1	G2	G1/G2	P	G1	G2	G1/G2	P
Low	-	-	-		9283	427912	0.02	+	844	494607	0.002	-
	-	-	-		-	-	-		26405	407562	0.060	+
Med	11017	72403	0.15	+	5889	2008521	0.003	?	2292	1481238	0.002	?
	3247	183176	0.02	?	1553	1192003	0.001	?	791	614882	0.001	-
High	-	-	-	-	-	-	-	-	2959	385255	0.008	?
	80285	13335365	0.06	+	3439	2588180	0.001	?	177	110087	0.002	-

Key G1 first glow, G2 second glow, G1/G2 glow ratio, P = ++ v.strong peak + peak ? shoulder - no evidence of peak

Table 5.1 TL results for Paprika

Ginger

Concentration: 10% Spike

Mat	Low				Medium				High			
	G1	G2	G1/G2	P	G1	G2	G1/G2	P	G1	G2	G1/G2	P
Low	8918	6199753	0.001	?	1330	476397	0.003	?	104026	4071419	0.03	++
	1597	2521680	0.001	?	30263	1651734	0.02	+	32216031	1003986	32	++
Med	37737	23689	1.6	+	11306	363700	0.03	+	3214325	264219	12	++
	24882	17660	1.4	+	73221	8324	8.7	+	702387	42742	16	++
High	33092	160789	0.2	+	-	-	-	-	3594578	1593043	2.2	++
	29691	1302027	0.02	+	18860	27350	0.7	?	959256	440645	2.2	++

Concentration: 1% Spike

Mat	Low				Medium				High			
	G1	G2	G1/G2	P	G1	G2	G1/G2	P	G1	G2	G1/G2	P
Low	1004	105948	0.01	-	2492	53033	0.05	?	2515659	222095	11	+
	1430	93007	0.02	-	3490	1854382	0.002	?	90869	282769	0.3	+
Med	2211	432065	0.005	?	1414	125053	0.01	-	22395	30877	0.7	+
	84	42006	0.001	-	1939	105341	0.02	-	2924961	856870	3.4	+
High	3195	4156197	0.001	-	13124	6696683	0.002	?	51039	478002	0.1	+
	3412	4725662	0.001	-	91658	142842	0.6	+	166966	1082707	0.2	+

Concentration:0.1% Spike

Mat	Low				Medium				High			
	G1	G2	G1/G2	P	G1	G2	G1/G2	P	G1	G2	G1/G2	P
Low	1471	3992	0.4	+	-	-	-		-	-	-	
	737	11675	0.06	-	302	3410953	0.001	-	140975	75971	1.9	+
Med	1497	54953	0.03	?	5355455	374852	14	+	10696	349295	0.03	+
	573	93614	0.01	?	572	98843	0.006	-	1322	64256	0.02	-
High	2943	1458690	0.002	-	1893	72804	0.03	-	6758	3755372	0.002	?
	1478	853955	0.002	-	8473	4414639	0.002	-	32905	37702	0.9	+

Key G1 first glow, G2 second glow, G1/G2 glow ratio, P = ++ v.strong peak + peak ? shoulder - no evidence of peak

Table 5.2 TL results for Ginger

Cinnamon

Concentration: 10% Spike

Mat	Low				Medium				High			
	G1	G2	G1/G2	P	G1	G2	G1/G2	P	G1	G2	G1/G2	P
Low	346521	866993	0.4	+	82470	138100	0.6	+	727431	147305	4.9	++
	43653	252632	0.2	+	1876809	205830	9.1	+	1216630	147221	8.2	++
								+				
Med	444975	538351	0.8	+	204851	89139	2.3	+	9229835	3098945	3.0	++
	69632	29625	2.4	+	293267	176303	1.7	+	842293	301789	3.0	++
High	450205	778503	0.1	+	43507	475583	0.1	+	548167	393914	1.4	++
	245228	683524	0.2	+	50976	345107	0.1	+	487302	674597	0.7	++

Concentration: 1% Spike

Mat	Low				Medium				High			
	G1	G2	G1/G2	P	G1	G2	G1/G2	P	G1	G2	G1/G2	P
Low	17624	555843	0.03	+	32358	349953	0.1	+	11207	72078	0.2	+
	11075	422731	0.03	+	83193	1056012	0.1	+	101764	101320	1.0	+
Med	23985	87090	0.3	+	104894	178107	0.6	+	281	8476	0.03	-
	14030	64749	0.2	+	24084	171807	0.2	+	29962	199022	0.2	+
High	1861	139819	0.01	?	28295	156440	0.02	+	26845	250558	0.1	+
	22027	1005387	0.02	+	45031	5753993	0.01	+	6860	106181	0.06	+

Concentration:0.1% Spike

Mat	Low				Medium				High			
	G1	G2	G1/G2	P	G1	G2	G1/G2	P	G1	G2	G1/G2	P
Low	1690	14361	0.1	?	362	20492	0.02	-	796354	205956	3.9	+
	1766	121198	0.01	?	15248	968497	0.02	+	2778	61021	0.05	+
Med	20906	264809	0.08	+	2480	818707	0.003	?	3146	93974	0.03	+
	991	7242	0.1	+	474	46283	0.01	-	35570	212799	0.2	+
High	3430	398229	0.01	?	5799	817176	0.01	?	5276	136853	0.04	+
	30253	3722787	0.01	+	10650	842080	0.01	+	91589	612162	0.15	+

Key G1 first glow, G2 second glow, G1/G2 glow ratio, P = ++ v.strong peak + peak ? shoulder - no evidence of peak

Table 5.3 TL results for Cinnamon

Sage

Concentration: 10%

Spike

Mat	Low				Medium				High			
	G1	G2	G1/G2	P	G1	G2	G1/G2	P	G1	G2	G1/G2	P
Low	1173616	3073895	0.4	++	44871	2930148	0.02	+	1993611	4318569	0.5	+
	83101	396678	0.2	++	26539	2075096	0.01	+	628677	1334726	0.5	+
Med	808478	1157630	0.7	++	116988	903146	0.1	++	156322	151996	1.0	+
	659328	1254794	0.5	++	79920	416995	0.2	++	130973	52254	2.5	+
High	331526	13888147	0.3	++	79849	3343518	0.02	+	118559	610676	0.2	+
	392357	3345659	0.1	++	12935	1274910	0.01	+	465548	1181700	0.4	+

Concentration: 1%

Spike

Mat	Low				Medium				High			
	G1	G2	G1/G2	P	G1	G2	G1/G2	P	G1	G2	G1/G2	P
Low	16506	241739	0.07	+	914	17053	0.050	?	10206	466716	0.02	+
	45686	192885	0.24	+	3722	552181	.01	?	43315	1447748	0.03	+
Med	10133	343632	0.03	+	18916	613938	0.03	+	30615	264848	0.12	+
	3872	450068	0.01	+	692	74727	0.01	?	73041	202953	0.4	+
High	80709	2018012	0.04	+	23933	2754196	0.01	?	5123	386961	0.01	?
	85286	2656479	0.03	+	16183	1105348	0.02	?	70984	1632261	0.04	+

Concentration:0.1%

Spike

Mat	Low				Medium				High			
	G1	G2	G1/G2	P	G1	G2	G1/G2	P	G1	G2	G1/G2	P
Low	1750	867920	0.002	?	587	691645	0.001	-	11057	1187875	0.01	?
	12484	578872	0.022	+	6214	2447551	0.003	-	1513	344314	0.004	?
Med	648	48490	0.010	-	2405	820712	0.003	?	5838	1520120	0.004	?
	1618	670870	0.002	-	905	230124	0.003	?	7350	816020	0.009	+
High	22914	5653489	0.004	+	1179	168670	0.07	-	10456	3970	2.6	+
	3881	650454	0.006	-	4439	139997	0.03	?	8640	1428452	0.01	+

Key G1 first glow, G2 second glow, G1/G2 glow ratio, P = ++ v.strong peak + peak ? shoulder - no evidence of peak

Table 5.4 TL results for Sage

Basil

Concentration: 10% Spike

Mat	Low				Medium				High			
	G1	G2	G1/G2	P	G1	G2	G1/G2	P	G1	G2	G1/G2	P
Low	192964	492152	0.4	++	73500	392958	0.2	+	16445	83718	0.2	+
	190531	319030	0.6	++	960929	136252 1	0.7	+	64613	246	262	+
Med	1157302	915210	1.3	++	18829	41837	0.5	+	180037	121112	1.5	+
	2483673	1248763	1.9	++	80403	345876	0.2	+	740378	419959	1.8	+
High	27469	154438	0.2	+	353136	538501	0.7	+	24155	175779	0.1	+
	67910	368233	0.2	+	56811	742178	0.1	+	21076	205519	0.1	+

Concentration: 1% Spike

Mat	Low				Medium				High			
	G1	G2	G1/G2	P	G1	G2	G1/G2	P	G1	G2	G1/G2	P
Low	280	163196	0.002	-	251	32050	0.01	-	6104	54449	0.1	+
	703	2512	0.3	-	7366	608030	0.01	+	9547	557270	0.02	+
Med	510699	904732	0.6	+	32601	37831	0.9	+	37587	279933	0.1	+
	252087	418399	0.6	+	15735	497434	0.03	+	37676	46718	0.8	+
High	284	123841	0.002	-	9358	264031	0.04	+	1763	877557	0.002	?
	4545	237464	0.02	?	666	351331	0.002	?	8564	553847	0.02	+

Concentration:0.1% Spike

Mat	Low				Medium				High			
	G1	G2	G1/G2	P	G1	G2	G1/G2	P	G1	G2	G1/G2	P
Low	11156	348618	0.03	+	206	67708	0.003	-	1757	218610	0.01	?
	2204	222843	0.01	+	94	46151	0.002	-	16615	1793801	0.01	+
Med	45763	166208	0.2	+	30114	902875	0.03	+	28288	70721	0.4	+
	50704	157292	0.3	+	17842	97751	0.2	+	72591	117633	0.6	+
High	388	263338	0.001	-	517	280358	0.002	-	204	50769	0.004	-
	75	220444	0.003	-	494	74801	0.007	-	218	388357	0.001	-

Key G1 first glow, G2 second glow, G1/G2 glow ratio, P = ++ v.strong peak + peak ? shoulder - no evidence of peak

Table 5.5 TL results for Basil

Oregano

Concentration: 10% Spike

M	Low				Medium				High			
	G1	G2	G1/G2	P	G1	G2	G1/G2	P	G1	G2	G1/G2	P
L	114006	166902	0.7	++	1161880	3386404	0.3	++	352803	822862	0.4	+
	1784391	2112423	0.8	++	1695179	548056	3.1	++	87191	349242	0.3	+
M	470353	1451631	0.3	++	765262	6773960	0.1	+	5646527	3108655	1.8	+
	442913	493778	0.9	++	342322	2618254	0.1	+	742742	1363315	0.5	+
H	1630212	10228039	0.2	++	100695	925793	0.1	+	58377	830611	0.07	+
	327839	3204138	0.1	+	1483778	5221066	0.3	++	89279	1714064	0.05	+

Concentration: 1% Spike

Mat	Low				Medium				High			
	G1	G2	G1/G2	P	G1	G2	G1/G2	P	G1	G2	G1/G2	P
Low	176807	1524530	0.1	+	103890	2763654	0.04	+	1119	868247	0.001	?
	46493	1271155	0.04	+	138224	1051434	0.13	+	8686	1220210	0.01	+
Med	318872	4127718	0.08	+	13058	889329	0.01	?	682470	2094195	0.3	+
	125583	2046243	0.06	+	3897	286458	0.01	?	534318	9626483	0.1	+
High	142797	4273446	0.03	+	13392	2151716	0.01	?	2029	280456	0.01	-
	624841	7275103	0.09	+	24368	6462481	0.004	?	1107	212143	0.01	-

Concentration:0.1% Spike

Mat	Low				Medium				High			
	G1	G2	G1/G2	P	G1	G2	G1/G2	P	G1	G2	G1/G2	P
Low	9889	2057999	0.005	+	2118	946357	0.002	?	4776	1474406	0.003	-
	8507	2378456	0.004	+	39105	1167419	0.03	+	23240	864820	0.03	+
Med	13693	1679033	0.01	+	4014	1898973	0.002	?	2773	127819	0.02	?
	19497	1001459	0.02	+	3912	695317	0.006	?	1425	405268	0.004	?
High	1499	966624	0.002	-	1412	637542	0.002	-	25646	798655	0.32	+
	1136	414624	0.003	?	45669	695317	0.07	+	10517	657107	0.02	+

Key G1 first glow, G2 second glow, G1/G2 glow ratio, P = ++ v.strong peak + peak ? shoulder - no evidence of peak

Table 5.6 TL results for Oregano

5.4 TL performance for all products

A total of 324 TL measurement was conducted, with eight samples requiring repeat analysis due to their data being associated with specific analytical problems. Combined results for all six products are shown below (Table 5.7). Classification of samples were identified using the criteria set out in the standard method EN1788 (1998). Samples with glow ratios greater than 0.1 and dominant peak in the defined temperature interval were identified as positive. The TL results in the columns marked P+G1/G2<0.1 would have be indicative of a blended sample. Using standard criteria these are, however, identified as either unirradiated or requiring repeat analysis.

For the 10% concentration case, for all matrix sensitivities with low sensitivity spike, 92% of the total analysis were identified as irradiated with 8% identified as unirradiated using the standard criteria. For all matrices with medium spike; 97% were correctly identified as irradiated and 3% identified as unirradiated. For those matrices with high spike, 100% were identified correctly as being irradiated. The results at 10% concentration therefore do show an improvement with increasing spike sensitivity, as expected. The majority of the samples (>96%) can be detected using EN1788 1998 criteria.

All matrices, at 1% concentration, with low spike sensitivities, 69% of analysis were identified as irradiated and the remaining 31% unirradiated, using 1998 criteria. Those matrices with medium spike sensitivity, 72% were identified as irradiated and 28% were identified as unirradiated. High spike to all matrices gave an 83% identification rate for an irradiated sample. Again, therefore, an increasing proportion of blends can be detected with increasing sensitivity of the irradiated component; the average proportion across all sensitivity bands being 75%.

64% of samples were identified at 0.1% concentration for low spiked matrices. The use of medium spike with all matrices produced a 36% identification of an irradiated sample. For those matrices spiked with high sensitivity, 61% of these mixes were identified using the standard method. In this case the dependence on spike sensitivity is less pronounced; no doubt reflecting the increased sub-sampling variabilities of these low concentration blends. On average 54% of these products are detectable using 1998 EN1788 criteria.

Figure 5.4 shows a graphical presentation of the overall TL results for each of the products using the CEN EN1998 classification criteria. It is noticeable that at the 10% concentration, detection for all three sensitivity cases for both spike and matrix, is exceptionally good. Again as with the PSL results, we observe that for both the 1% and 0.1% concentration the detection rate has decreased. Note that a significant proportion of samples showing peaks in the low temperature region have G1/G2 < 0.1, and therefore would be problematic under any formal identification scheme suggested so far.
For comparison Figure 5.5 shows the same data analysed relative to the EN1788

Method	Criteria	0.1%	1%	10%
PSL	Intermediate & positive	**33%** 18/54	**69%** 37/54	**100%** 54/54
TL (1996)	G1/G2>0.1 + P	**15%** 15/100	**35%** 38/108	**84%** 91/108
TL (1998)	Peak	**54%** 54/100	**75%** 81/108	**96%** 104/108

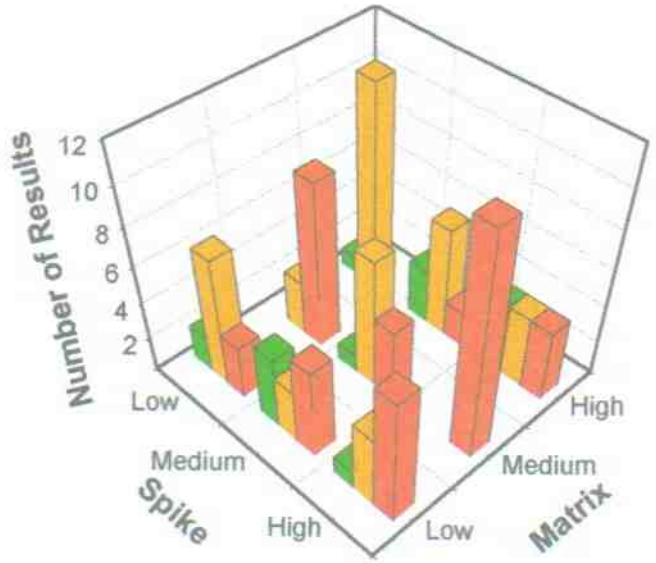
Table 5.8 Percentage detected or identified for further investigation for all products (orange and red bands)

(1996) criteria. Here the proportion of samples satisfying the G1/G2 > 0.5 criteria is very low - confirming the importance of extending the use of peak identification as embossed in the 1998 proposal.

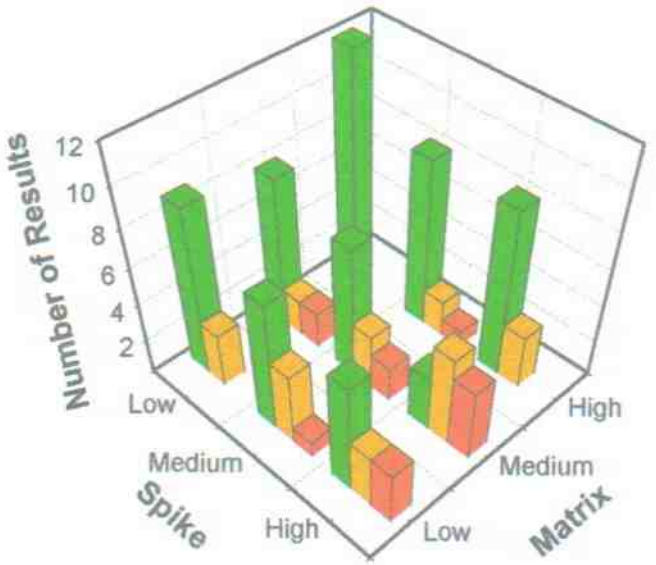
The overall detection and non-detection rates from both PSL and TL analyses are summarised further in Tables 5.8 and 5.9

Method	Criteria	0.1%	1%	10%
PSL	Negative<700counts/s	**67%** 36/54	**31%** 17/54	**0%** 0/54
TL (1996)	G1/G2<0.1	**85%** 85/100	**65%** 70/108	**16%** 17/108
TL (1998)	G1/G2<0.1 nopeak	**46%** 46/100	**25%** 27/108	**4%** 4/108

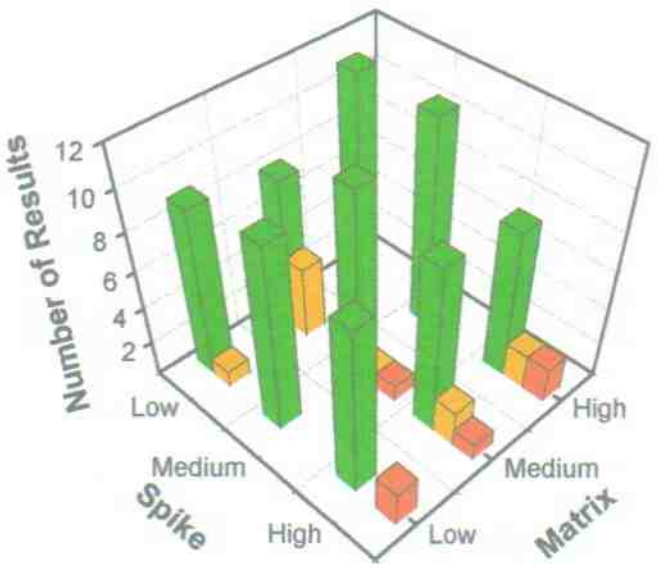
Table 5.9 Percentage not detected for all products (green band)



10% Concentration



1% Concentration



0.1% Concentration

CEN EN1788 1996 CRITERIA

- G1/G2>0.5 + P
- G1/G2<0.5>0.1 + P
- G1/G2<0.1

Figure 5.5 TL results for all herb and spice samples using EN1788 1996

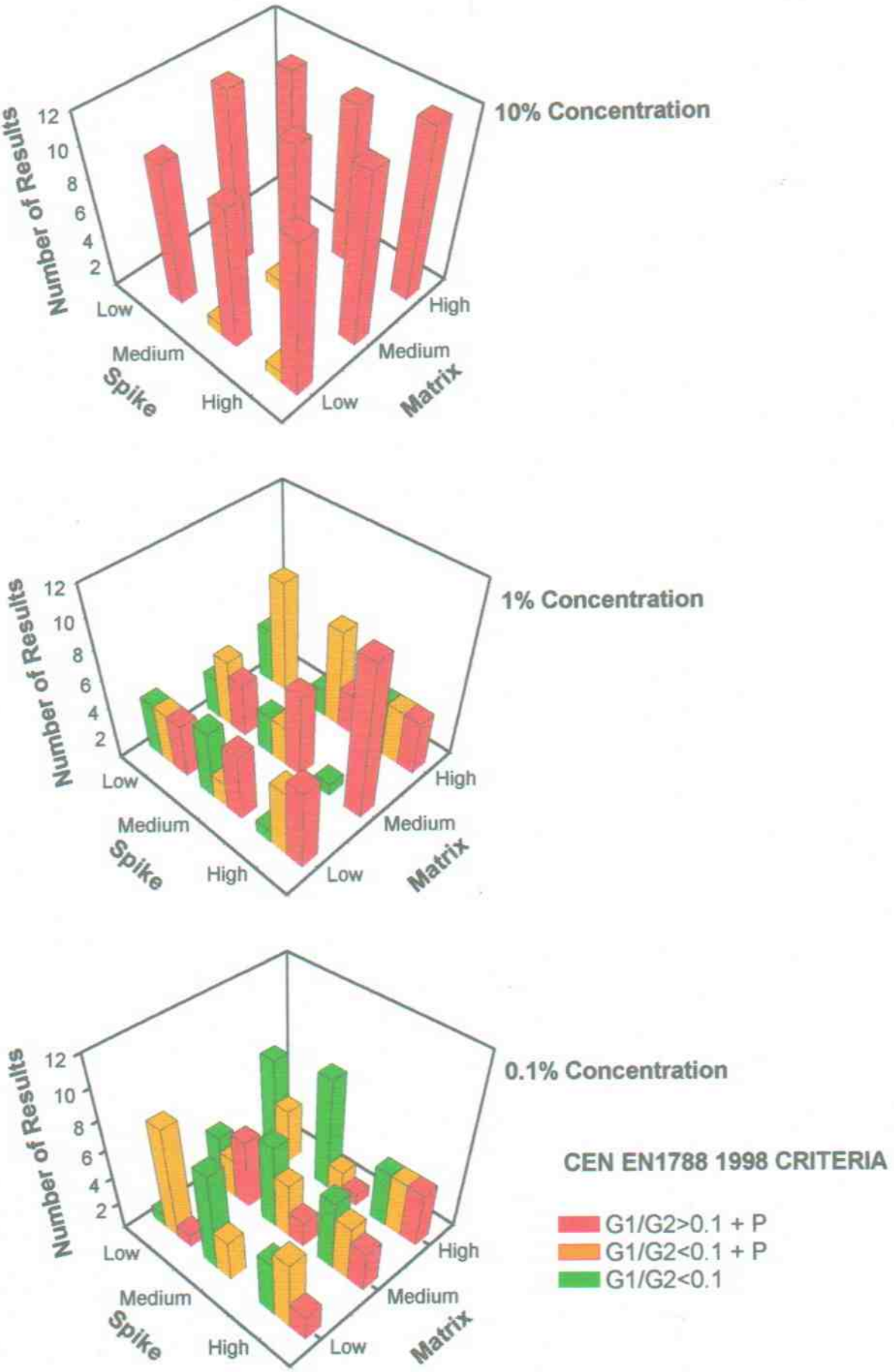


Figure 8 TL results for all herb and spice samples using EN1788 1998

Figure 5.4 TL results for all herb and spice samples using EN1788 1998

Concentration: 10% Spike

Mat	Low			Medium			High			Total		
	+ve	-ve	P+R<0.1	+ve	-ve	P+R<0.1	+ve	-ve	P+R<0.1	+ve	-ve	P+R<0.1
Low	10	2	-	10	1	1	11	0	1	31	3	2
Med	12	-	-	11	0	1	12	0	0	35	0	1
High	11	1	-	11	0	0	12	0	0	34	1	0
Total	33	3	-	32	1	2	35	0	1	100	4	3

Concentration: 1% Spike

Matrix	Low			Medium			High			Total		
	+ve	-ve	P+R<0.1	+ve	-ve	P+R<0.1	+ve	-ve	P+R<0.1	+ve	-ve	P+R<0.1
Low	4	4	4	5	5	2	6	1	5	15	10	11
Medium	4	3	5	6	3	3	11	1	0	21	7	8
High	0	4	8	3	2	7	4	4	4	7	10	19
Total	8	11	17	14	10	12	21	6	9	43	27	38

Concentration: 0.1% Spike

Matrix	Low			Medium			High			Total		
	+ve	-ve	P+R<0.1	+ve	-ve	P+R<0.1	+ve	-ve	P+R<0.1	+ve	-ve	P+R<0.1
Low	1	1	8	0	7	3	2	4	5	3	12	16
Medium	5	4	3	2	6	4	3	5	4	10	15	11
High	0	7	4	1	8	2	4	4	4	5	19	10
Total	6	12	16	3	21	9	9	13	13	18	46	37

+ve = Glow ratio greater than 0.1 and peak -ve = glow ratio less than 0.1 and no peak P+G1/G2<0.1 = Glow ratio less than 0.1 evidence of a peak (either a shoulder or a strong peak)

Table 5.7 TL performance for all products carried out in duplicate

6. Summary and Conclusions

Project FS 1925 was a preliminary investigation of the impact of blending on the detection of irradiated herbs and spices using luminescence methods. Herb and spice products, are probably most common product to be treated with radiation, as this provides an effective means of reducing microbial load. Individual herbs and spices are traded without prejudice to the organoleptic qualities of the product. Several tonnes of consolidated batches of material from various sources; and the possibility arises that some of these batches, contain mixtures of irradiated and unirradiated material. Due to their diverse origins, irradiated herbs and spices can find their way into dilute mixtures in the food supply chain. Thus results in a different set of analytical problems from those associated with detecting pure irradiated products.

UK and European validated luminescence methods for detecting irradiated foods have been developed on pure products. The validated methods (TL) use classification criteria based on glow ratio thresholds and glow shape indicators. In the cases of blended products the problem is the response of an irradiated component in a dilution mixture containing several different sensitivities from irradiated and unirradiated components. For many of these cases the glow ratio thresholds are not satisfied and the glow shapes have many individual elements. Standard detection methods do not address this problem and there is a need to evaluate the extent to which luminescence methods falls short with regards to blended products.

This project has set out to establish the effect of introducing a minor irradiated component on the detection rate. The study has been designed to introduction pure irradiated material at three concentration levels; 10%, 1% and 0.1%, into a range of unirradiated matrices. Luminescence sensitivities have been shown to widely vary and three sensitivity cases were identified for both the unirradiated matrix and irradiated component. The sensitivities were defined using calPSL measurements, and put into three categories of high, medium and low sensitivities, giving rise to 27 blended samples for each pure product. The six pure products; paprika, cinnamon, ginger, basil, oregano and sage were selected.

A series of experiments were set up to optimise the mixing method and the effects of mixing and timing using PSL throughout for quality checks. Homogeneity was checked, again using PSL, on all unirradiated and irradiated pure products. Screening PSL was carried out on subsamples of the three concentration cases, with both matrix and spike sensitivity cases, to establish the system's performance with blended products. Screening PSL, at the 10% concentration case, gave no negative results for all products and sensitivity cases. 69% screened into the positive band, with 31% giving an intermediate signal, suggesting further investigation. For all products at 1% concentration, only 20% of the total measurements produced a positive result. 31% gave a negative result with the remaining 48%, an intermediate signal was measured. No positive results at 0.1% concentration for all products and sensitivities were recorded. 67% gave negative results and the remaining 33% were recorded as intermediate.

Standard EN1788 (1998) TL analysis was carried out on duplicate aliquots of the six products, resulting in a total of 324 TL analysis. The TL results were examined using standard interpretation and classification schemes. For a product to be identified as irradiated; the glow ratio must be greater than 0.1 and that the sample exhibits a peak in the predefined temperature band. The TL results for all six products at the 10% concentration level, correctly identified 96% of the total analysis. The remaining 4%, identified as unirradiated, did however show evidence of an irradiated component in the first glow curve. At 1% concentration, only 75% were identified as being irradiated with the detection rate at 0.1% concentration decreasing to 54% using standard criteria. The previous EN1788 (1996) criteria were consistently less robust, when faced with blended samples.

The TL results show that at 10% concentration, it is possible to detect with reasonable reliability the irradiated material using standard classification criteria. However, decreasing the concentration level, does reduce the ability of the classification criteria to identify approximately 50% of samples that contain an irradiated component.

Observations from the graphic presentation (Figures 5.5 and 5.6), of the overall results from both PSL and TL analyses, show that the concentration of irradiated material was more important than matrix or spike sensitivity in determining the analytical outcome. More detailed analysis of the data, however confirms that increasing sensitivity of the irradiated component and decreasing matrix sensitivity lead on average, to better performance. Individual cases can be found in the data sets which appear to counter this trend. This is mostly like to be due to incomplete mixing and the probability of separating irradiated minerals - a few milli grams from a 50g aliquot, is very low, especially at the lower concentration levels.

Current luminescence techniques rely on PSL and TL criteria established for pure products for absolute classification. Blended products have produced results which fail to satisfy international validation criteria. The results presented in this report recommend that further work is necessary to improve upon the present validated methods and their detection criteria as neither techniques when applied to blended products produce glow ratios which identify them as being irradiated and in many cases the standard classification criteria is not satisfied. The TL method does produce slightly better results than the PSL method and in the majority of the TL cases there is evidence of irradiation from the first glow. The results discussed in this report, indicate that there are areas where improvement to both PSL and TL methods, for blended products, is necessary, especially in the context of proposed EU labelling requirements and current commercial practices..

7. References

1. Statutory Instruments 1990,The Food (Control of Irradiation) Regulations 1990 SI 1990: 2490 HMSO

2. Statutory Instruments 1990, The Food Labelling (Amendment) (Irradiated Food) Regulations, 1990, SI 1990:2489

3. Statutory Instruments 1996, The Food Labelling Regulations 1996, SI 1996:1499, HMSO

4. EC, 1997, Common Position (EC) No 46/97, Official Journal of the European Communities, C389, 36-50, 22nd January 1997.

5. MAFF, 1992, Detection of Irradiated Herbs and Spices, MAFF validated methods for the Analysis of foodstuffs, V27, 16p, Ministry of Agriculture, Fisheries and Foods, Norwich.

6. MAFF,1993, MAFF validated methods for the analysis of Foodstuffs, V 27, Detection of Irradiated Herbs and Spices: Scottish Universities Research and Reactor Centre Procedure for Thermoluminescence Detection of Irradiated Herbs and Spices using renormalised separated minerals, J. Assoc. Publ. Analysts, 29, 187-200

7. EN, 1997, Foodstuffs - Detection of irradiated food from which silicate minerals can be isolated: Method by Thermoluminescence, BS EN 1788, BSI, London.

8. CEN, 1999, Detection of irradiated food using photostimulated luminescence, Draft EN standard. Working Document CEN TC275/WG8 N127

9. Sanderson D.C.W., Slater C., Cairns K.J, 1989,Detection of Irradiated Food, Nature 340,23-24

10. Sanderson D.C.W., Slater C., Cairns K.J.,1989, Thermoluminescence of Foods : Origins and Implications for detection of irradiation, Rad. Phys. Chem.,34,915-92

11. Sanderson D.C.W., Slater C., Cairns., K.J., 1989, Luminescence Identification of Irradiated Foods, Int. J. Rad. Biol.,55,5

12. D.C.W. Sanderson, 1990, Luminescence Detection of Irradiated Foods, in "Food Irradiation and the Chemist", ed. D.E. Johnston and M.H. Stevenson, Royal Society of Chemistry ISBN 0851868576, 25-56

13. Sanderson D.C.W., Carmichael L.A., Naylor J.D.,1996, Recent Advances in thermoluminescence and photostimulated luminescence detection methods for irradiated foods, in Detection Methods for Irradiated Foods, ed McMurray et al, Royal Society of Chemistry, Cambridge, 124-138

14. Sanderson D.C.W., 1991, Photostimulated luminescence (PSL): A new approach to identifying irradiated foods, in Potential new methods of detection of irradiated food, ed. Raffi J., Belliardo J.J., EUR 13331, 159-167.

15. Sanderson D.C.W., Carmichael L.A., Ni Riain S., Naylor J., Spencer J.Q.,1994, Luminescence Studies to Identify Irradiated Food, Food Science and Technology Today, 8(2),93-96

16. Sanderson D.C.W., Carmichael L.A., Naylor J.D., 1995, Photostimulated luminescence and thermoluminescence techniques for the detection of irradiated food, FSTT 9(3), 150-154

17. Sanderson D.C.W., Carmichael L.A., Fisk S., 1998, Establishing Luminescence Methods to detect irradiated foods, FSTT 12(2), 97-102

18. Sanderson D.C.W., Carmichael L.A., Fisk S., 1997, An International Collaborative Blind Trial of Thermoluminescence Detection of Irradiated Fruits and Vegetables, Final Report : MAFF 1B073, accepted for JAPA

19. Sanderson D.C.W., Carmichael L.A., Fisk S., 1997, An International Collaborative Blind Trial of Thermoluminescence Detection of Irradiated Shellfish, Final Report : MAFF 1B073, accepted for JAPA

20. Sanderson D.C.W., Carmichael L.A., Fisk S., 1997, An International Collaborative Blind Trial of Photostimulated Luminescence Detection of Irradiated Shellfish, Final Report : MAFF 1B073, accepted for JAPA

21. Sanderson D.C.W., Carmichael L.A., Fisk S., 1997, An International Collaborative Blind Trial of Photostimulated Luminescence Detection of Irradiated Herbs, Spices, and Seasonings, Final Report : MAFF 1B073, accepted for JAPA

22.Working Party on Food Authenticity, Ministry of Agriculture, Fisheries and Food. Undeclared Irradiation of Foodstuffs. Draft Report June 1997.