

# A GUIDE TO SPECTRORADIOMETRY Instruments & Applications for the Ultraviolet

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Spectroradiometry is the technique of measuring the spectrum of radiation emitted by a source. In order to do this the radiation must be separated into its component wavebands and each band measured separately. A graph of intensity against wavelength will then provide a picture of the spectral characteristics of the source. Looking at a rainbow is a very crude form of spectroradiometry: raindrops aligned along the same axis reflect the wavelengths of radiation from the sun at different angles, and the eye detects the bands of coloured light that "unsorted" were white sunlight (fig.1). The same effect is achieved looking through a prism or by using a diffraction grating, both of which are used in spectroradiometers to split the radiation entering the system into its constituent wavebands. A suitable detector is then used to quantify the radiation of each wavelength (Box 1).

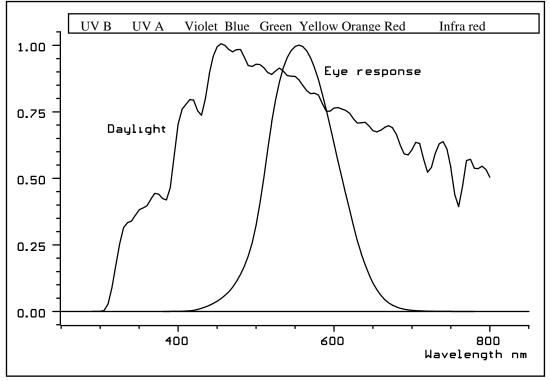


Fig. 1 Typical Daylight Spectrum Superimposed with Photopic Response

The measured radiation may be expressed in a number of ways, depending upon how the radiation entering the spectroradiometer is collected, and how it is processed by the system software. A spectroradiometer makes an objective, physical measurement in radiometric units at each wavelength, but this may be converted into a more subjective photometric equivalent which indicates how the radiation is perceived by the eye: its luminous quality. Box 2 gives a definition of radiometric quantities and their photometric equivalents. The response of a typical eye to radiation of different wavelengths (fig.1) is well known (ref. Hunt R.G.W., Measuring Colour) so knowing the spectral radiometric properties of a source allows the photometric equivalent to be calculated.

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The electromagnetic spectrum is classified into broad bands according to its main source (e.g. gamma rays are nuclear in origin, infra-red radiation is produced by molecules and hot bodies), and specified by the wavelength ( $\lambda$ ) or frequency (v) of the radiation (fig.2). All electromagnetic radiation travels at the speed of light (c = 3 x 10<sup>8</sup> ms<sup>-1</sup>) in a vacuum and

$$c = \lambda v$$

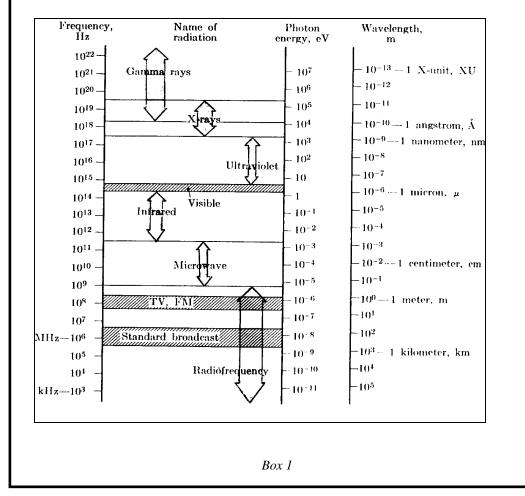
therefore either wavelength or frequency will uniquely identify the radiation.

In addition to considering electromagnetic radiation as a wave with a wavelength and a frequency (number of waves passing a point per second), it can also be thought of as a stream of particles, called photons, each of which carries an amount of energy

E = hv

where h is Planck's constant ( $6.6256 \times 10^{-34}$  Js). The energy carried by a photon is the energy that it can give to matter which it encounters, and thus determines the response that the radiation may invoke: e.g. photons of ultraviolet radiation have energies of the same order of magnitude as the energies involved in many chemical reactions, thus there are many chemical and biological responses to irradiation by ultraviolet radiation.

Spectroradiometry is concerned with the precise determination of radiation at much greater resolution than the broadband classifications. Radiation will be referred to by its wavelength in this text, the corresponding frequencies and photon energies are given in figure 2.



Spectroradiometry has many uses in the laboratory, in the environment, in industry and in the medical world, from identification and quantification of chemical constituents to quality control and safety assessments.

UV Spectroradiometry Bentham Instruments Ltd

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Precisely determining the emission spectrum of a source provides information about the emitting substance as different elements emit radiation at characteristic wavelengths when they change between the discreet energy states that they can occupy and emit photons corresponding to the energy gaps (Box 1). The inverse of this process, the characteristic absorption of radiation by matter, can also be used for identification by looking for absorption lines after a broad spectrum of radiation has passed through a substance (e.g. the Fraunhofer lines of the sun), or for quantifying the amount of the substance by the strength of the absorption lines. For example, the absorption of solar ultraviolet radiation at different wavelengths is used to calculate the amount of ozone in the atmosphere by comparing the relative intensities of wavelengths which are strongly and weakly absorbed by ozone as they pass through the atmosphere to the earth's surface.

Radiometric quantity	S.I. unit	Definition	Photometric quantity	S.I. unit
Radiant flux	watt W	Total power emitted by a source	Luminous flux	lumen lm
Radiant intensity	W / sr	Flux emitted per unit solid angle	Luminous intensity	candela cd
Radiance	W / (sr.m²)	Flux emitted per unit of observed area	Luminance	cd / m <sup>2</sup>
Irradiance	$W \ / \ m^2$	Flux density received by a surface	Illuminance	lux

Table 1 Radiometric / photometric quantities

Both radiometric and photometric specifications of radiation are commonly used and should not be confused. Radiometry refers to total power, important for energy considerations e.g. solar power. Photometry refers to "light" i.e. radiation as seen by the eye, and is a measure of the illumination provided by a source. A very powerful source may provide little illumination if it emits its power at wavelengths outside the visible waveband (400-700nm).

#### Box 2

Alternatively, knowledge of a radiation source may be required to assess its efficiency (or safety) for a particular task: phototherapy, suntanning, growth chambers, public lighting etc. Knowing the spectrum of radiation emitted by a source enables calculation of its chemical or biological effect on a system whose action spectrum (response to radiation of different wavelengths) is already well known. This has been discussed for vision (Box 2) which is important enough to have its own terminology and units. Other common biological action spectra are those for erythema (sunburn) and DNA damage, both in the ultraviolet (UV) region, or the photosynthetically active radiation in the visible (Fig.3).

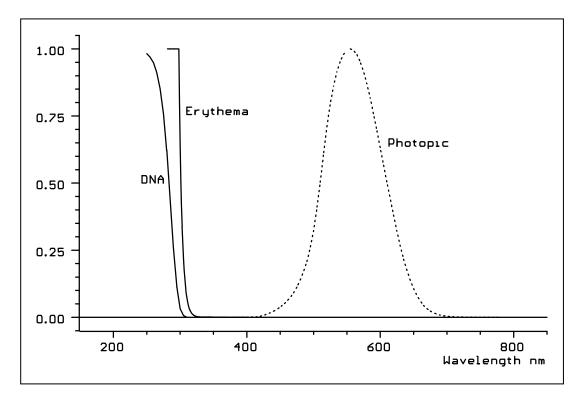


Fig. 3 Some Common Action Spectra

The choice of spectroradiometer, its components and specifications, will depend very much on the use for which it is intended. The general features of a spectroradiometric system are discussed in chapter 2.

Any spectroradiometer system will consist of four basic units (Fig.4):

- 1) The input optics which gather radiation from a specified field of view and deliver it to the monochromator.
- 2) A monochromator which separates the radiation into its component wavelengths.
- 3) A detector which measures the radiation at each wavelength.
- 4) A control and logging system to define the data gathered and store it.

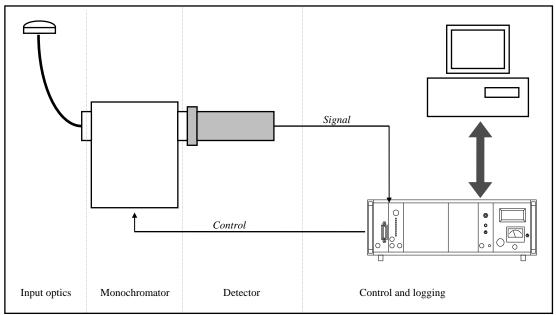


Fig. 4 Basic Components of a Spectroradiometer System

Each unit may be one of a number of different options, and the combination of units must be chosen to match the proposed use of the complete instrument. When choosing a spectroradiometer the first thing to determine is the performance that will be expected of the instrument. Table 2 shows the basic performance criteria which must be considered (see Box 3 for a glossary of terms), the major elements of the system which determine the performance, and some typical requirements for the measurement of solar UV radiation, one of the most demanding spectroradiometric tasks.

	Performance	Determining element	Solar UV reqmt.
1	Wavelength range	Grating / prism and detector	280-400nm
2	Wavelength resolution	Grating/prism and slit function	<= 1 nm
3	Sensitivity and dynamic range	Detector and overall throughput of system	>6 O of M
4	Straylight rejection	Single/double monochromator, slit function	$10 e^{-8}$ double
5	Field of view	Input optics	Cosine response
6	Operating environment	Thermally stable? Weatherproof? Rugged?	All desirable

Glossary of terms			
Cosine response	A beam of radiation of power P normally incident to a surface will have an intensity of I $Wm^2$ at the surface. If that same beam reaches the surface from an incident angle $\theta$ to the normal then the intensity at the surface will be Icos $\theta$ $Wm^2$ because the power P is spread over a wider area (figure 7). When measuring radiation on a horizontal surface with a 2 pi field of view the receiving optics are often required to have a cosine response i.e. to transmit to the monochromator the integrated incident radiation from the whole hemisphere with radiation from each incident angle conforming to the above rule and not being over- or underrepresented due to the optical properties of the receiver. In practice this is difficult to achieve, especially at large $\theta$ , and the response of a "cosine" receiver should be tested so that errors due to imperfect adherence to the above rule can be assessed. In theory integrating spheres should have perfect cosine responses, but practical limitations on their construction often prevent this.		
Diffraction grating	A surface (plane or concave) covered with a high density of parallel lines which produces wavelength dependent angular dispersion of incident radiation. Ruled plane gratings are produced by ruling the lines onto a master grating with a diamond tool and then duplicating other gratings in a manner similar to the production of compact disks. Holographic plane gratings and concave gratings are produced by a holographic process.		
Dynamic range	The range of intensities that a system can measure, usually expressed as a power of 10, that is a number of orders of magnitude.		
Field of view	Describes the region of the surrounding sphere from which the instrument receives radiation: what the instrument "sees". Some common geometries measure: irradiance arriving on a horizontal surface from the hemisphere above (2 pi FOV); a stated narrow FOV, e.g. 1 degree is often used to look at the sun's disk and measure direct solar radiation; to measure the total radiant flux of a source it is enclosed in an integrating sphere to give a 4 pi FOV.		
Integrating sphere	Integrating spheres are spheres internally coated with a highly reflective material to form a very smooth surface. Radiation entering the sphere is reflected multiple times before falling on an exit port. At this stage the radiation does not "know" where it has come from and a measurement made at the exit port is independent of the original incident angle of the radiation. This is true for a large sphere with small ports. In practice the size of the sphere is often limited and the ports are proportionally too large so that at some incident angles radiation can pass directly from entrance to exit port. This can be remedied by baffles within the sphere but usually reduces the compliance of the sphere to the ideal cosine response. To measure total radiant flux a source can be placed inside a sphere of suitable dimensions and all radiation emitted by the source will then be reflected inside the sphere and finally reach the exit port where it is measured.		
Resolution	The smallest incremental change in wavelength that can be resolved and measured. This depends upon the physical control of the grating(s) which determines the wavelength step size possible, and on the slit function which determines the sharpness of the image at each step. Broad images sampled close together will overlap and produce a smoothed spectrum whose small structure has not been resolved.		
Sensitivity	The lowest level of irradiance, or change in irradiance. that can be measured. A very sensitive instrument is often sensitive to electrical noise, temperature etc. as well as radiation and must be operated in a controlled environment. Sensitivity is not to be equated with accuracy.		

Slit function	The shape of a single monochromatic line measured by the instrument as it scans across a waveband centred on the wavelength of the line. This is usually approximately triangular in shape with the apex at the wavelength of the incident monochromatic wavelength and indicates the near field straylight properties of the monochromator (figure 6). The slit function is often described by its width at half the maximum intensity, the full width half maximum (FWHM). This is not always sufficient to determine the importance of straylight in an instrument as broad "wings" to the slit function can be important if measuring a source whose intensity changes very rapidly with wavelength (e.g. solar UVB radiation).
Straylight	Radiation at wavelengths other than the one being measured that enters the detector at the same time and is attributed to the wavelength of measurement ( $\lambda$ m). Straylight can be near field (from wavelengths close to $\lambda$ m) as a result of the instrument slit function, or far field (from wavelengths outside the immediate vicinity of $\lambda$ m) from misguided radiation within the monochromator. Double monochromators are less susceptible to straylight than single monochromators because of the additional dispersion and baffling between gratings.

Box 3

#### 2.1 <u>The Monochromator</u>

The central unit of a spectroradiometer is the monochromator whose basic elements are shown in Figure 5 for a double monochromator. A single monochromator has only one grating and a central slit is therefore not required. Either single or double monochromators usually have mirrors for directing the radiation and baffles to help reduce straylight.

Within the monochromator the first element to select is that which will separate the radiation into its distinct wavebands, a task which may be performed by a prism or a diffraction grating. The most common dispersers are diffraction gratings because although prisms are more robust, gratings have a number of optical advantages:

- a) Radiation must pass through a prism and will inevitably be attenuated (this is a particular problem in the UV) while the optically active part of a grating is only the front surface so there are virtually no attenuation losses.
- b) A prism cannot be "tuned" to provide its best performance over a particular waveband, whereas gratings can be tailored to optimise their performance in the desired way by changing the shape and spacing of the grooves. The spacing of the grooves (or lines) determines the dispersion as:

 $\begin{array}{rl} \sin\theta = & n\lambda/2d \\ & \text{where } \theta \text{ is the angular dispersion} \\ & \lambda \text{ is the wavelength} \\ & d \text{ is the separation of the lines} \\ & n \text{ is the order of dispersion (usually the first order).} \end{array}$ 

Therefore, the more lines/mm (smaller d) the better the dispersion (larger  $\theta$ ), and hence the higher the resolution.

The shape of the grooves can be adjusted to optimise grating performance at a specified wavelength, the grating is then said to be blazed at that wavelength.

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For use in the UV, gratings are commonly blazed at 250nm with 2400 lines/mm.

c) The angular dispersion of a prism is often not linear, especially at the extremes of the spectrum where the radiation is exiting close to the corners of the prism. This can be corrected with additional imaging optics but is an added complication.

Even with diffraction gratings further imaging of the dispersed radiation may be needed to provide a flat field of view for detection. This will depend upon the type of grating used and the tolerance of the instrument specifications. A plane grating produces a curved spectral field which can be redirected onto the slit of the monochromator in a flattened form by using a concave mirror. Again this is front surface optics which involves negligible attenuation, and also has the advantage that the substrate of the mirror does not have to be a high grade material. Alternatively a concave holographic grating may be used to both disperse and produce flat field radiation, but in trying to do two jobs at once, the grating will introduce some degree of astigmatism (curvature in the lines that make up the spectral image). If a straight line image is required on the exit slit of the monochromator then more optical processing is necessary.

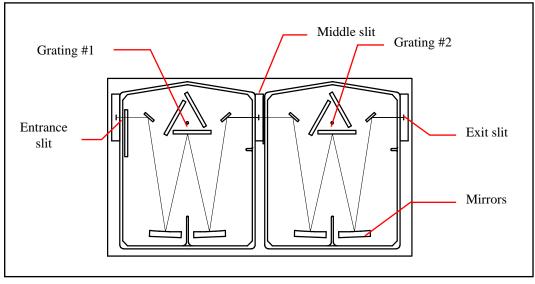


Fig. 5 Elements of a Double Monochromator

The disperser often has to be mounted so that it can be rotted under very precise control to direct each wavelength in turn onto the detector (this is not the case if the detector is a diode array). If there are two gratings they must be rotated in exact synchronisation. This can be achieved by mechanically linking them together, or by careful control of each separate mounting drive. To avoid backlash of the grating drive mechanism introducing uncertainty in the wavelength alignment most spectrometers scan the spectrum in only one direction, usually from short to long wavelengths. The grating movement is frequently under computer control although some systems have a manual override. As resolution requirements increase, so the demands on precision and repeatability of wavelength specification and alignment also increase, together with the requirement for wide and pure dispersion, and rigorous rejection of straylight.

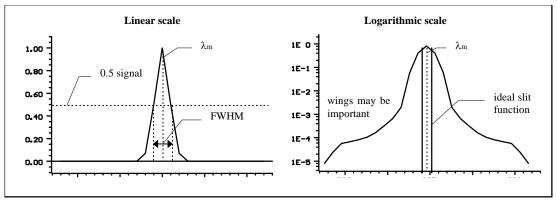


Fig. 6 The Slit Function

There are a number of sources of straylight within a monochromator. The slit function of an instrument is in large part a function of the physical slit widths and the performance of the grating, thus narrower slits should help to reduce near field straylight. However, there are also disadvantages to using extremely narrow slits: the throughput of the monochromator decreases necessitating a more sensitive detector, and the instrument becomes increasingly sensitive to temperature change, mechanical shock etc. A balance must therefore be found between slit width and sensitivity. Far-field straylight has several possible causes which result in radiation being diffusely reflected around the interior walls and fixtures of the monochromator until some of it reaches the exit slit and the detector. A first preventative measure against this is to paint all internal surfaces matt black (with a paint which does not outgas and cause absorption). Following this, precautions should be taken to restrict sources of straylight, simple examples of which are overfilling optical components, or imperfections in those components. Overfilling gratings or mirrors (directing radiation onto more than the active optical surface) leaves 'spare' radiation as a possible contributor to straylight. This can be remedied by using baffles near the monochromator entrance to prevent radiation entering the system over too wide an angle. Scratches or imperfections on mirrors or gratings cause unwanted scattering of radiation which may find its way to the detector. It is not always possible to eliminate sources of straylight, but an operator should understand the straylight characteristics of the instrument, and be able to accept them for a given application.

Double monochromators, with their additional dispersion and baffling, generally have a much better rejection of straylight than single monochromators.

# 2.2 <u>Input Optics</u>

The radiation that enters the monochromator, and where it comes from, will depend upon the input optics. Radiation may be required from a restricted angular field of view for which a well baffled tube or telescope may be used, from the whole upper hemisphere (common for environmental measurements) by way of a cosine diffuser or integrating sphere, or from all around (4 pi) using an integrating sphere. The material used for lenses, diffusers, or filters will determine the waveband of radiation which will reach the monochromator, for example glass cannot be used when measuring short wavelength UV radiation: quartz lenses, optical fibres etc. are needed. Teflon is frequently used as a diffuser for UV measurements, while integrating spheres may be coated with barium sulphate or manufactured from p.t.f.e. type material.

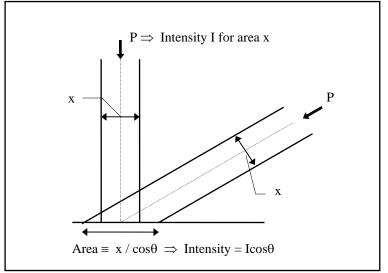


Fig. 7 The Cosine Response

Input optics must be tailored to suit the needs of the operator, not only for optical properties but also for other practical considerations. It is often desirable to have the receiving surface some distance from the monochromator, in which case the radiation must be reliably directed from one to the other. In a fixed environment this may be achieved with mirrors, but a more flexible solution is to use a light guide, either liquid or a bundle of fibres. Such light guides will attenuate radiation, but the majority of the loss is at the ends of the guide, so guides of several meters attenuate little more than guides of only one meter.

## 2.3 <u>The Detector</u>

Having gathered radiation from the desired field of view and separated it into its component wavelengths, the next task is to measure the intensity at each designated wavelength. The detector used for this measurement will be determined by the wavelength range, dynamic range and sensitivity required of the measurements. The basic detector technologies fall into three groups: photoemissive detectors (e.g. photomultiplier tubes), semiconductor devices (e.g. silicon either as a single detector or an array), and thermal detectors (e.g. thermopile). Within each type there are many options and modes of operation available.

Thermal detectors respond to radiation of all wavelengths. They work by absorbing the incident radiation, resulting in a temperature rise which can then be measured in a number of ways. A common method is to use two dissimilar metals connected in series, a thermocouple. One junction is exposed to radiation and heats up, the other acts as an unexposed reference. The temperature difference between the two junctions generates a voltage (proportional to  $\Delta T$  and hence proportional to incident radiation) which can be measured. To increase the voltage output a number of thermocouples can be joined

together in series. Such a thermopile is frequently used for measuring total radiation across a broad waveband e.g. in solarimeters for measuring total solar radiation, or net radiometers which measure solar and terrestrial (long wave infra red) radiation. If the incoming radiation is chopped or pulsed then a pyroelectric detector may be used. Pyroelectric materials have an inherent electric polarisation. When heated the material expands and the polarisation changes, building up a charge on opposite faces of the material. Connecting the two surfaces causes a current flow which can be measured. Pyroelectric detectors can respond to changes in radiation more rapidly than thermocouples, and because they respond to a *change* in temperature they are not affected by steady background radiation.

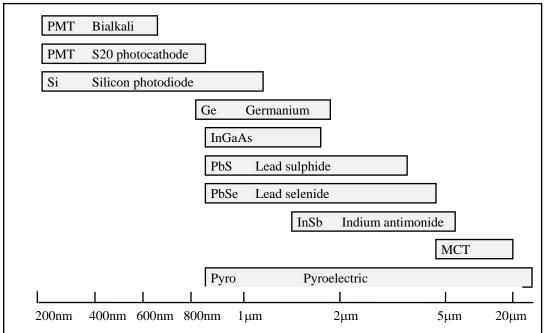


Fig. 8 Wavelength Ranges of Different Detector Types

Photoemissive and semiconductor detectors (Box 4) have more restricted wavebands of detection than thermal detectors. Fig.8 shows some typical detection wavebands for photomultiplier tubes and semiconductors. This can be an asset as radiation outside the detection band can be ignored when considering background radiation and straylight. Within the waveband of detector response the sensitivity of both types of device is generally greater than that of thermal detectors (with photomultipliers being orders of magnitude more sensitive than semiconductors), but is also wavelength dependent. This is because detection begins with a direct photon-electron interaction which depends on photon energy, and the number of incident photons. Each device will have a peak of responsivity with decreasing response at longer and shorter wavelengths. At long wavelengths the cut-off in response occurs when the photon energy is too low to initiate the reaction leading to detection. At short wavelengths the response to power ratio decreases because there are fewer incident photons per watt, and the photons may be absorbed before they reach the sensitive area of the detector. Ultraviolet radiation is strongly absorbed by the coatings on semiconductors, and by detector windows if they are not made of quartz.

#### **Photomultipliers and Semiconductors**

The vacuum photodiode is the basic photoemissive device upon which a photomultiplier is built. It consists of a photocathode and an anode inside an evacuated envelope. Photons of sufficient energy incident on the photocathode free an electron and provide it with kinetic energy from any "spare" energy not used in the freeing process. If the electron has enough kinetic energy it can escape from the surface of the cathode. A voltage applied between cathode and anode causes the emitted electrons to flow and creates a current which can be measured. The current is proportional to the intensity of the incident radiation over 6-8 orders of magnitude.

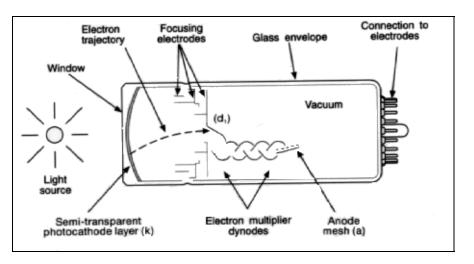


Fig. 9 Schematic Operation of a pmt (Thorn EMI Electron Tubes Ltd)

A photomultiplier tube is a combination of a vacuum photodiode and an electron multiplier (Fig.9). Between the cathode and anode of the vacuum photodiode is a chain of dynodes at ever increasing potential. Electrons reaching each dynode are multiplied by secondary emission so that one electron leaving the photocathode becomes hundreds or thousands of electrons at the anode. This process is an almost noise free amplification and increases the sensitivity of the detector enormously.

Photomultipliers are the most sensitive detectors in the near UV and visible but have the disadvantages of being relatively bulky and requiring a stable high voltage supply.

Semiconductor devices work in a number of different ways depending upon the material of which they are made, but all rely on photoconductivity. In bulk photoconductive detectors (e.g. lead sulphide and lead selenide which respond to near infra red radiation) the absorbed photons produce free charge carriers in the material, changing the electrical conductivity. Applying a voltage across the material causes a current to flow which is proportional to the incident radiation. The other type of semiconductor device is the junction detector (or photodiode) which can be operated in photovoltaic mode or photoconductive mode (with a reverse bias applied). Junction detectors (silicon, germanium indium arsenide) have p-n junctions in the material and when a photon is absorbed near a p-n junction a hole-electron pair is produced. These pairs migrate to opposite sides of the junction producing a voltage (photovoltaic mode), and current in a connected circuit. If a reverse bias is applied across the p-n junction then the electron-hole pairs increase the conductance of the material (photoconductive mode) and the current from the bias plus the free carriers is proportional to the incident radiation. The most common junction detector for radiation measurement is the silicon photodiode. The spectral response of silicon covers the visible and near infra red, and can be UV enhanced (Fig.10). The linearity and dynamic range of the silicon are excellent and the device is easy to use. Box 4

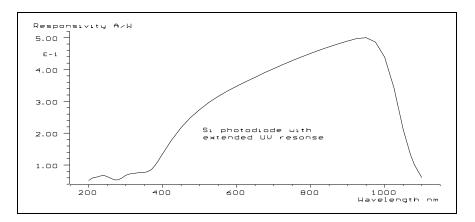


Fig. 10 Spectral Response of Silicon Photodiode

The response time of photomultipliers and semiconductors is very rapid because they depend on direct photon-electron interaction (Box 4), an advantage for rapidly changing signals or when a fast scan is required across a range of wavelengths. The sampling time at a given wavelength can be specified for each type of detector (with a suitable control system) to optimise the balance between signal level and speed: at low signal levels sampling time can be increased to improve detection and signal to noise ratio. For a "snapshot" picture of a spectrum, rather than a scanned measurement made over a finite time, an array of diodes may be used. The concept is simple: the dispersed radiation from a monochromator is allowed to fall on a line of small semiconductor detector elements constructed as an integrated circuit such that each element receives radiation from a narrow waveband. Each detector element is then sampled by computer, a data acquisition process that takes only milliseconds. In practice diode array detectors are not suitable for all applications. Although they have the advantage of speed, and negate the need for moving parts to scan in a spectroradiometer, the requisite balance between straylight rejection, resolution and signal to noise ratio for some types of measurement (e.g. solar UVB) cannot easily be achieved.

In addition to the data requirements of a scan, the operating environment should also be considered when selecting a detector. Photomultiplier tubes are the most sensitive detectors in the UV and visible by several orders of magnitude, but they require a specialised power supply and are not as rugged as the semiconductor devices. They are also temperature sensitive so for accurate measurements in a changing environment they should be temperature stabilised. If there is no need to measure short wavelength UV, and there is ample radiation available, then semiconductor detectors are simpler to use and more rugged.

## 2.4 <u>The Control and Logging System</u>

The control and data logging associated with spectroradiometers are tasks most often performed by a personal computer, although this need not be the case. The method of control, the devices and communication lines between computer and monochromator, and between detector output and computer or other logger, should be optimised to match the desired features of the system as a whole. Amplifiers and analogue to digital converters are frequently required as first stages of signal processing, and these should be designed to cope with the expected range and magnitude of the raw signal to be measured. The power and speed of today's computer systems means that sophisticated control and data processing is possible in less than the time taken for the monochromator system to respond to commands. This means that scan speed is usually hardware rather than software limited, and the use of diode arrays for gathering instantaneous spectra is possible. The commercially available software packages supplied with spectroradiometer systems can offer the general user a lot of versatility, but specialised options remain the responsibility of the individual operator. Regardless of the technical excellence of a spectroradiometric system the data that it produces will only be as good as the calibration of the instrument. The calibration is the means by which a voltage or current signal (or other measurable quantity) from the detector is converted into radiation units. A rigorous calibration should identify not only the wavelength dependent numerical conversion factors, but also any conditions which may lead to changes in those factors, e.g. temperature. If a system appears to be temperature sensitive then it can either be stabilised, calibrated and used at a set temperature, or the temperature sensitivity can be determined, the temperature can be monitored, and a correction applied to standardise all measurements at the temperature of calibration.

There are two basic ways to perform the basic calibration for conversion factors. One is to measure a source of well defined output and equate the signal from the spectroradiometer with the known output of the source at each wavelength to produce a series of calibration factors. The other method is to use a second well calibrated or standard instrument and compare the response of the two instruments to a single source. The source need not be well defined so long as both instruments measure it in exactly the same manner at the same time. The ease, precision, stability and frequency of the calibration procedure is once again determined by the waveband of radiation to be measured and the mode and environment in which the spectroradiometer is to be used.

In practice, most operators calibrate their instruments using a standard source of the radiation parameter which they then wish to measure (e.g. total radiant flux or irradiance). Standard sources are obtainable from national calibration laboratories e.g. National Physical Laboratory (NPL, UK), National Institute of Standards and Technology (NIST, USA), Physikalisch-Technische Bundesanstalt (PTB, Germany), or may be calibrated by other certified laboratories and "traceable to" one or other of the national standards laboratories. Bentham Instruments Ltd supplies a range of calibration standards traceable to NPL (table 3).

Bentham model no.	Standard of	Wavelength range	Units	Photometric units
SRS8	Spectral radiance	380nm - 2500nm	mW / (sr.m <sup>2</sup> .nm)	$cd / m^2$
SRS8/RI	Spectral radiant intensity	380nm - 2500nm	mW / (sr.nm)	cd
CL2	Spectral irradiance	300nm - 2500nm	mW / (m <sup>2</sup> .nm)	lux
CL3	Spectral irradince	200nm - 400nm	mW / (m <sup>2</sup> .nm)	n/a
TSRF	Spectral total radiant flux	300nm - 2500nm	mW / nm	lumens

#### Table 3 Example Calibration Standards from Bentham

The sources are supplied with a calibration certificate: a list of the output at a series of wavelengths (interpolation is used to find the output at intermediate wavelengths), an indication of the overall error in the stated output at each wavelength, and the conditions under which these figures were determined. As an example, for standards of spectral

irradiance the latter should include details of the distance between lamp and detector and the reference point for determining this distance, the exact current supply to the lamp and the polarity with which it should be delivered, the orientation of the lamp with respect to the detector, and also whether it is to be used horizontal or vertical. Primary standards are generally used with the lamp in the vertical position, but some secondary standards are seasoned and calibrated in the horizontal position, and in future primary standards may become available for this mode of operation.

It is very important that when a lamp is used for calibration purposes it is used in the same manner as that specified for the original determination of its output characteristics. The irradiance from a source follows the inverse square law so correct distancing of the source and the reference surface of the input optics is vital. For a lamp at a typical calibration distance of 50cm an error in distancing of 0.25cm will produce an error of 1% in irradiance. If the standard distance is smaller then distancing is even more critical. The lamp and spectroradiometer foreoptics should also be correctly aligned perpendicular to a line joining them, according to instructions supplied with the lamp (often, but not always, the centre point of the lamp filament is aligned with the centre of the input optics). One surface of the lamp is usually specified as the one to face towards the spectroradiometer. If either lamp or receiving surface is not perpendicular to the axis between them further errors can be incurred, of the order of 1-2% for a rotation of 5 deg. of the receiving surface. A transverse displacement from the lamp-optics axis of 2cm would give an error of the order 1% in the measured irradiance, while rotating the lamp about its own axis can result in errors of up to 1% per degree. Careful positioning and alignment is therefore a vital first step towards a good calibration.

With the lamp in position it requires power, which should be supplied with the correct polarity and at the correct (and precisely controlled) level. Reversing the polarity of supply to a lamp can significantly change its output even when the current supply is stable as resistance of the filament (and hence temperature and irradiance) may be different. In addition, the change is likely to be wavelength dependent. A typical operating current for a 1000W tungsten halogen standard of spectral irradiance is 8.0A, which should be maintained at a level of single mAs or better if changes in lamp output are to be less than 1%, especially at short (UVB)wavelengths. Monitoring the current to, and voltage across, a standard lamp while in use will enable changes in lamp performance to be detected. It also allows the operator to determine when the lamp has warmed up and reached the steady state required for calibration. Without this information a warm up time of 30 minutes is generally recommended for 1000W lamps, the time may be less for lamps of lower wattage.

A good calibration depends on more than just good lamp and instrument operation, attention must also be paid to the environment in which the calibration is performed. In a laboratory the surroundings should be designed to minimise the risk of straylight reaching the spectroradiometer by reflection from local surfaces (walls, ceiling, bench, optical fixtures). Prevention often means painting all possible surfaces black or running black curtains around the calibration area, and using correctly designed baffles where necessary. Ventilation should also be carefully considered. Unless the laboratory is large the room can become very warm with prolonged use of a powerful lamp and some heat extraction is desirable, especially if the spectroradiometer is not independently temperature stabilised. However, ventilation at a level discernible by the operator (|2ms^1 or more) can cool the lamp and decrease its radiance.

Ventilation becomes more of a problem if calibrations are to be performed with the instrument in situ outdoors. Secondary lamps of low wattage (e.g.100W) are usually used for such field calibrations and bring with them an inherently greater uncertainty than that associated with primary standards. They must be mounted in an internally blackened housing whose combination of size, heat sinks and ventilation will ensure that the lamp always operates at one temperature and is not subject to overheating at high ambient temperatures, or cooling in windy and/or low ambient temperature conditions. Radiation from the surroundings must also be excluded from the lamp - spectroradiometer radiation path. This is not easy to achieve in practice but field calibrations (or checks) have the advantage of allowing the instrument performance to be verified in the normal operating position, and ensure that movement of the spectroradiometer from laboratory to field has not changed the initial calibration.

Before an absolute calibration is attempted the wavelength alignment of the spectroradiometer must be checked. This can be done by scanning the output of a mercury lamp (or other source with well defined emission peaks) and determining the wavelength of peak emission of several of the lines. Misalignment in the wavelength determination can itself be wavelength dependent so several emission lines spanning the proposed range of measurement should be checked. Correction, if necessary, can then be applied in a wavelength dependent manner, or more simply with a single wavelength shift for the whole spectrum if this will not cause the acceptable tolerance on wavelength alignment to be exceeded. If operating outdoors the Fraunhofer lines in the solar spectrum can be used for this check.

## 3.1 <u>Lamps</u>

The final consideration, or more correctly the first decision to make, is which lamp to use for a calibration source. Ideally the emission spectrum and intensity of the calibration lamp should be similar to the experimental source which the instrument will then measure. In practice this is not always possible, but a calibration source of approximately the same intensity as the expected measurements in the waveband of importance should be selected, otherwise great faith is being placed in the long range linearity of the detector system. Low irradiance from the lamp at unmeasured wavelengths is also desirable to avoid straylight (external or internal to the instrument) influencing the calibration. Intensity of radiation at the spectroradiometer input can be determined through selection of lamp power and distancing. Calibration sources are available for spectral radiance, spectral irradiance and total irradiance, and fall into two main categories: arc lamps and quartz tungsten halogen (QTH) lamps.

QTH lamps have a doped tungsten filament enclosed in a quartz envelope which is filled with a rare gas and a small amount of halogen. The filament is heated to over 3000K by the current flowing through it, producing white light, and evaporating the tungsten which is deposited on the inside of the quartz envelope. The evaporation thins the filament and blackens the wall of the bulb so that radiation output is gradually reduced. However, the addition of halogen inside the bulb reverses much of this process as the halogen effectively removes the tungsten from the envelope and redeposits it on the filament. This halogen cycle keeps the envelope clean, increases lamp life and improves the long term stability of the lamp. The spectrum produced by a QTH lamp is a smooth continuum with intensity increasing as wavelength increases from the longer wavelength UV through the visible and into the near infra red (Fig.11). The lamps have a high visible output, good stability and are easy to use across a broad spectral range.

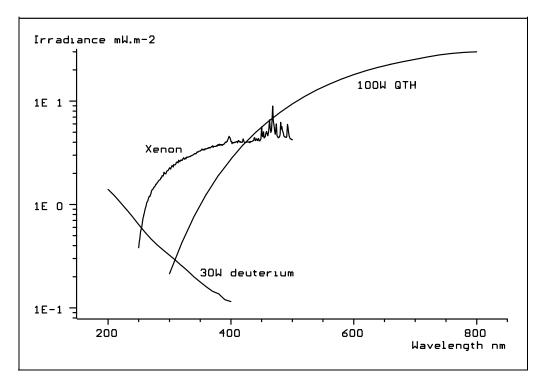


Fig. 11 Spectral Irradiance of Typical Deuterium, QTH and Xe lamps

Arc lamps are of either the high or low pressure type. An example of the low pressure arc is the deuterium lamp. Electrical arcing between an anode and cathode in the bulb produces radiation from the deuterium gas which fills the envelope at low pressure. Deuterium lamps have a high output in the UV region which is continuous and decreasing from 180nm to about 350nm. At longer wavelengths the output spectrum has much more structure (Fig.11). High pressure arc lamps (e.g. xenon or mercury) have a very small arc region between anode and cathode, producing high intensity radiation from what is essentially a point source. The lamps are filled with rare gas at several atmospheres pressure, or a little rare gas and an exact amount of mercury. During operation of the lamps the internal pressure increases to several tens of bar (typical atmospheric pressure is about 1 bar), requiring special precautions for handling and operating the lamps. A large part of the output of high pressure arc lamps is at short wavelengths, and the type of quartz forming the envelope can be used to restrict emission of some of the shortest wavelengths. Xenon lamps have a correlated colour temperature of about 6000K, similar to the sun (Fig.11).

Calibration in the UV, especially if intending to measure solar UVB radiation, is not a simple proposition. The lamp which most closely resembles the shape and intensity of the solar spectrum, at least in the UV, is the xenon lamp, but this is not generally considered stable enough to be used as a standard calibration lamp. The choice of primary standard becomes either the quartz tungsten halogen (DXW or FEL type), or the deuterium lamp, or both. The deuterium lamp has a better UV output at wavelengths < 310nm, while the QTH is better at longer wavelengths and into the visible, although both are about two orders of magnitude less intense than a xenon lamp (sun) of the same power at 300nm. If both types of lamp are available a cross-over calibration can be made using the deuterium at UVC wavelengths, the QTH for the visible and UVA, and both to provide continuity

through the UVB region. If only one lamp can be selected then the QTH offers a smooth spectral output through the visible waveband and provides adequate radiance in the UVB.

Whichever lamp(s) is selected for calibration purposes the correct safety procedures must be observed. High pressure arc lamps require the most stringent precautions: because of the risk of explosion they should always be operated in a fully enclosed housing. Even when cold the internal lamp pressure is greater than the surroundings and heavy gloves plus eye wear or a face shield should be used for handling purposes. For lamps that emit radiation at wavelengths < 200nm ozone will be produced. This is a toxic gas and correct ventilation should be employed to remove the ozone from the working environment. All the lamps mentioned emit UVB and varying amounts of UVC radiation, wavelengths which are biologically damaging. Eyes and skin likely to be exposed to the radiation should be protected and the operator should not look directly at the lamp nor spend more time than necessary in close proximity to a burning lamp.

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Some of the most demanding applications of spectroradiometric measurements are those associated with environmental issues, because of the additional problems of measuring outdoors, or in space. The most challenging ground-based measurement is probably the determination of solar UV radiation and in particular the UVB part of the spectrum. UVB radiation represents the shortest wavelengths of radiation to reach the surface of the earth from the sun, and thus the most energetic photons naturally available to interact with biological, chemical and inanimate systems. Many reactions are initiated by UVB photons, a large number (but not all) of which are harmful to the irradiated system. The best known UVB effects are those which have direct implications for human health, most notoriously sunburn and skin cancer, but also cataracts, snow blindness, and an increasing concern about UVB effects on part of the immune system. A beneficial health effect of solar UVB radiation is the initiation of cutaneous vitamin D synthesis, a lack of which is associated with the diseases of rickets and osteomalacia. UVB also has detrimental effects on some types of plants and aquatic life, and accelerates the ageing of numerous paints, polymers and materials.

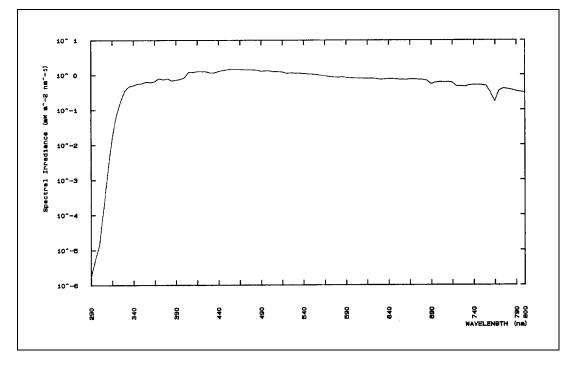


Fig. 12 Daylight with Overcast Sky (February, England)

Life on earth copes with, and even uses, the available UVB, but if the normal incident UVB changes rapidly then some systems may be unable to tolerate the additional harmful radiation and more of the damaging effects will become apparent. One example of this is the increase in skin cancer in the past couple of decades as a result not of environmental change in incident radiation, but of social change as people travel to sunnier climes and seek an all-over suntan. A change in the UVB climate is potentially far more important because it will affect all the biological systems that cannot choose their level of sun exposure and cannot protect themselves, implying changes in the competitive balance between UV sensitive and UV tolerant species, with knock-on effects which could alter

whole ecosystems. Just such a climate change would result from widespread ozone depletion in the stratosphere. Ozone and oxygen in the upper atmosphere absorb all the solar UVC radiation, but as ozone absorption of radiation decreases with increasing wavelength through the UVB part of the spectrum more and more photons penetrate the ozone layer and reach the biosphere. This gives the ground level solar spectrum its characteristic steep shoulder at the short wavelength end (Fig. 12) with intensity increasing by several orders of magnitude from the shortest detectable wavelength (>290nm, dependent on location and season) to the long wavelength UVB at 320nm. Reducing the amount of ozone would disproportionately increase the amount of the shorter (and more harmful) UV wavelengths and extend the solar spectrum towards the short wavelengths / high photon energies. Severe springtime ozone depletion and increased UVB radiation over Antarctica has been recognised for the past decade, and the role of man-made chlorofluorocarbons in this depletion has been acknowledged in the international agreement to phase out the use of these environmentally damaging chemicals (The Montreal Protocol, and amendments). Antarctica is unique in the combination of atmospheric conditions that occur there in early spring and lead to the observed dramatic ozone depletion, but low ozone has also been observed over other parts of the globe, including much of the Northern hemisphere. This was most significant in the years 1992 and 1993 following the eruption of Mount Pinatubo which injected aerosols into the stratosphere with the potential to alter stratospheric chemistry and upset the natural balance of ozone formation and destruction. In addition, the meteorological conditions in those years was unusual and would in any case have lead to ozone values on the low side of the widely variable climatological range. "High" UVB radiation was observed to coincide with the low ozone at a few locations, but there are no long-term UVB measurements to form a climatology against which the current measurements can be assessed, or to help identify future trends in incident UVB. The chlorine loading in the stratosphere is projected to continue increasing into the early years of the next millennium, and by implication the loss of ozone and an increase in UVB radiation at the earth's surface. However, our understanding of atmospheric chemistry is incomplete, other pollutants in the lower atmosphere can also influence the UVB reaching the surface, and other facets of climate change (e.g. a change in cloudiness) could have more affect than a small change in stratospheric ozone. Given all this uncertainty, and the potential damage to be caused by excess UVB, there are an increasing number of UV monitoring and research sites requiring the capability to make spectrally resolved measurements of solar UVB radiation.

Table 1 shows some of the performance requirements of a solar UV spectroradiometer, and figure 12 indicates why such stringent specifications are necessary. The wavelengths of most interest/concern are those with very low intensity, thus the instrument must be very sensitive. However, knowledge of the whole UVB (and usually UVA and maybe visible) spectrum is required for assessing total biological /chemical effectiveness of the sunlight, so the instrument must have a dynamic range capable of measuring intensities that vary by at least six orders of magnitude. Photomultiplier tubes are the most sensitive detectors for the UVB, and have the required dynamic range, but they do have other drawbacks (power supply requirement and temperature sensitivity) for the true field measurement.

The intensity of radiation increases so rapidly with wavelength that rigorous straylight rejection within the spectroradiometer is extremely important. A narrow slit function is essential for accurate determination of the shortest wavelength intensities: the broader the slit function the higher the apparent signal at short wavelengths due to near field straylight

from the adjacent but more intense longer wavelengths (Figure 13). A narrow slit function also increases resolution and enables the fine structure of a spectrum to be identified, as seen in Figure 13 where the solar spectrum was measured at the same time with two instruments having slit functions of FWHM 1.6nm and 0.5nm. Suppression of far field or background straylight within the spectroradiometer is also important because of the very low signal level in the UVB compared to the energy in the rest of the solar spectrum, a tiny fraction of which would provide sufficient background noise to prevent detection of the shortest wavelengths. It is this necessity to exclude all straylight which favours the use of double monochromators in solar UV spectroradiometers and has to date prevented widespread use of diode array detectors.

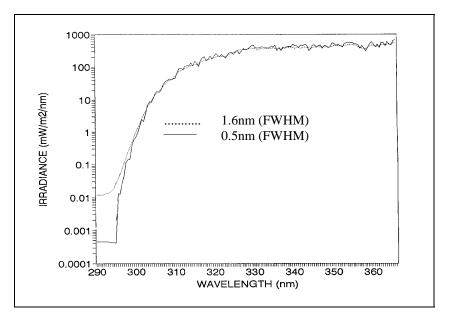


Fig. 13 Solar spectrum measured with different instrument slit functions

The most commonly requested measurement of solar radiation is for global radiation incident on a horizontal surface i.e. the input optics should have a cosine response with a 2 pi field of view above a horizontal plane, for which either an integrating sphere or a cosine diffuser (of Teflon or quartz) can be used. The other common input geometry allows direct solar radiation to be measured. The solar disk subtends to an angle of 0.54 degree when viewed from the earth's surface and the field of view often used for direct radiation measurements is 1 degree, encompassing a small amount of circumsolar radiation. Ideally the field of view of the direct radiation accessory should be flat over the required 1 degree with no detection outside this angle. In practice some radiation outside the required viewing angle is usually detected in a way analogous to the broadening of the ideal slit function by straylight. The narrow field of view can be achieved with careful baffling and / or focusing of the radiation entering the optical system through a narrow input aperture pointing directly at the sun. This type of measurement necessarily demands the ability to accurately track the sun, or at least the ability to align the input optics to the sun prior to a measurement. Direct spectral measurements can be used to assess column ozone thickness, aerosol optical depth, and the amounts of other atmospheric constituents. Further diagnostic measurements can be made looking at the zenith, that is observing the sky vertically above the instrument with a narrow field of view optic.

The same techniques are used in other areas of investigation and at other wavelengths to extract information about a system, or induce a controlled response. For example, the red/far red ratio (660 / 730nm) is used in plant research and development. The phytochromes, which control such development processes as flowering, stem elongation, leaf abscission (autumn leaf loss) and dormancy, are in turn controlled by the red/far red ratio of the irradiating light source. The red / far red ratio changes through the day, providing a daylength signal (e.g. for leaf loss in deciduous plants) and with position in a canopy (shaded or not) etc. In glasshouse cultivation developmental stages can be advanced or retarded by irradiating the plants with the correct ratios of red and far red radiation at certain times of day (or night). Thus, for example, flowers can be brought to bloom earlier or later than normal in the year, to commercial advantage.

Accurate measurements in the field require that the spectroradiometric system is not affected by changes in the external conditions: it must be weatherproofed in some way and should either not respond to changing temperature, humidity, pressure etc., or should be protected against such changes, or should be so well characterised that corrections can be made for the changes (which must also be recorded at the time of any measurement). The simplest solution is often to house the spectroradiometer in a controlled environment enclosure (weatherproof and temperature stabilised) with only the input optics exposed to the elements and connected to the rest of the system by some sort of light guide. The permanence of the enclosure must be suited to the uses to which the instrument is to be put and for which the data is intended. The less an instrument is moved the more stability can be expected of its calibration and performance. If the data is to be used to determine a UVB climatology, and detect changes or trends away from this baseline reference then the long term stability of the wavelength and absolute calibrations of the spectroradiometer are vitally important. For other uses, e.g. determining ozone amounts only the relative intensity of radiation at different wavelengths is necessary and the requirements for absolute calibration are less stringent.

Much of the discussion of solar UV spectroradiometry also applies to the spectroradiometry of artificial sources which mimic the sun for medical, therapeutic or cosmetic treatments. Phototherapy is used to treat a variety of disorders from psoriasis to seasonal affective disorder (SAD), and the use of sunbeds to promote a "healthy" looking year round tan is popular in affluent parts of the world where sunshine is not a regular feature of the climate. The testing of artificial UV radiation sources needs the same sensitivity and adherence to calibration protocols as solar measurements, but for safety the wavelength range of the spectroradiometer should extend into the UVC part of the spectrum. Many artificial "UVB" light sources also emit significant amounts of UVC radiation, photons with higher energies and greater damage capabilities than UVB. Unless it is specifically needed for a specialised purpose the UVC should be totally excluded from the spectrum of radiation that is allowed to reach a person undergoing therapy or tanning. For suntanning purposes UVB radiation, especially the shorter wavelengths, can also be excluded as UVA radiation will produce a tan. As the lamps and the filters which tailor the final emitted spectrum will both change and degrade with time all exposure units should be regularly checked, and for therapy purposes the wavelength alignment and intensity of radiation for a given treatment should be carefully monitored to ensure that the correct doses are administered.

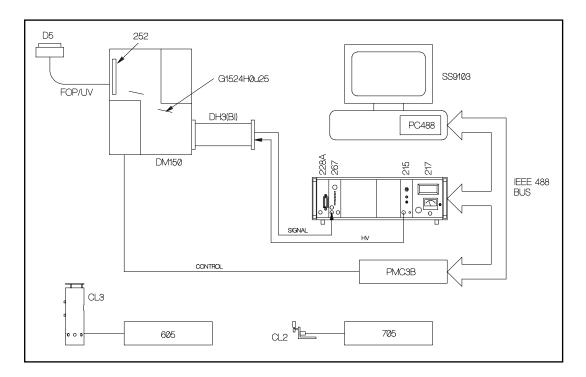


Fig. 14 Typical Bentham UV Spectroradiometer System

Sunlamp products are governed by legislation which is designed to "balance the need to limit acute (and delayed) damages from unintentionally long exposure and the need to provide for single exposure durations adequate to achieve and maintain a tan". This requires assessment of the maximum time for which a sunlamp can be operated to prevent severe sunburn, a calculation needing detailed spectral information of the lamps output, and documentation of the spectroradiometer used for the measurement. Health and safety legislation also governs the recommended exposure to other radiation sources e.g. intense radiation sources which can cause eye damage, from UV, visible or infra red radiation of sufficient intensity viewed for a long enough period. Testing of such sources requires a spectroradiometer covering the spectral range of the lamp output.

Not all spectroradiometric applications will demand the sophistication of solar UV measurement. A single monochromater and semiconductor detector with a correctly blazed grating will perform many tasks perfectly adequately and with much less fuss and cost. Choosing a spectroradiometer must begin with a careful analysis of the task to be performed, and then the best combination of components to achieve that task can be selected.

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Gardiner B.G. and Kirsch P.J. (Eds.) (1993) Second European Intercomparison of Ultraviolet Spectroradiometers. Commission of the European Communities Air Pollution Research Report 49

Gibson J.H., (Ed) Justification and Criteria for the Monitoring of Ultraviolet (UV) Radiation. Report of the UVB Measurements Workshop, Denver, Colorado 1991.

Kerr J.B. and McElroy CT (1993) Evidence for large upward trends of ultraviolet - B radiation linked to ozone depletion. Science 1032-1034.

McFarland, M and Kaye, J (1992) Chlorofluorocarbons and Ozone. Photochem. Photobiol. 55 (6) 911-929.

Passchier W.F. and Bosnjakovic B.F.M. (Eds) Human Exposure to Ultraviolet Radiation Risks and Regulations. Excerpta Medica, Amsterdam 1987.

Walker, J.H., Saunders, R.D., Jackson, J.K. and McSparron, D.A. (1987) *Spectral Irradiance Calibrations. NBS Special Publication* 250-20.

Webb,A.R, Gardiner,B.G., Blumthaler,M.,Forster,P., Huber,M. and Kirsch,P.J. (1994) A laboratory investigation of two ultraviolet spectroradiometers. Photochem.Photobiol. 60(1), 84-90.