Construction and testing of equipment using fluorescence for on-line monitoring of the distribution of recycled fibre during newsprint production

Johan Jason

Abstract

The use of recycled fibre in newsprint production affects the composition of the newsprint. This is due to paper additives, such as fillers and fluorescent whitening agents (FWAs), that are introduced in the newsprint via the recycled fibre. The more or less aged recycled fibres also affect the quality of the paper. This suggests a need of on-line monitoring of the distribution of recycled fibre during production.

In this project, portable optical equipment for such inspection has been developed and tested in laboratory environment. The equipment is based on detection of fluorescence principally from FWAs. Ultraviolet light is focused to a small, superficial volume in the paper, and detection of the fluorescence light from the excited volume is made around 450 nm. Tests of the signal response have been performed on paper samples containing different amounts of recycled fibre and other substances. The equipment has also been tested on a running web in the laboratory, demonstrating the possibilities of performing well-resolved, fast on-line measurements.

Keywords:
optical measurements, fluorescence, newsprint, recycled fibre

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1   Introduction

The use of recycled fibre in newsprint production has brought substances of otherwise limited use into the newsprint. Journal paper and fine paper, which make up a major part of the recycled paper, are furnished with special substances such as fillers and fluorescent whitening agents (FWAs). The presence of these substances in the recycled fibre may cause difficulties in maintaining the quality demands, especially when using large amounts of recycled fibre. Since the recycled fibre consists of more or less aged fibres, the paper strength may be affected.

These circumstances make it interesting to measure the distribution of recycled fibre and substances in newsprint during production. The information from such inspection, if performed on-line, may be used for process control resulting in a better paper quality.

In this diploma work, which is a part of a larger project involving the Division of Atomic Physics and the Swedish Newsprint Research Centre (TFL), equipment for on-line monitoring of the distribution of recycled fibre has been constructed and tested. The equipment, which is portable, uses fluorescence essentially from FWAs for detection of the recycled fibre along the paper web. A paper feeder, used in some of the tests, has also been constructed for the purpose of measuring on a running web in laboratory environment.

The first four chapters of the report deal with fundamental paper theory, especially newsprint and its composition. The emphasis is given to the optical properties of newsprint and of substances occuring in newsprint. In chapter 5 needs and possibilities of on-line distribution measurements are discussed on basis of the theory. This discussion is brought to practical matters in chapter 6, where the development and the construction of the equipment are described. The results from the optimisation and the basic testing of the equipment are given in chapter 7. Chapter 8 presents the results from measurements made on paper samples of varying composition. In chapter 9 the tests of the equipment on a running web are discussed. A description of the constructed paper feeder is also included. Finally, conclusions and future aspects are presented in chapter 10.

2 Natural and added substances in pulp and paper

2.1 Natural substances

Paper has a layered structure of more or less flattened wood fibres, which can be modified by treating the fibres in different ways during the pulp production. The size of a fibre depends on the kind of wood used and the season during which the fibre is formed, but generally speaking the length is of the magnitude 1-3 mm and the width about 20-40 μm. The fibres have narrowing ends and an inner cavity, the so called lumen, enclosed by a fibre wall with a thickness in the approximate range 3-10 μm. The fibre wall in turn consists of a number of layers, in which its main substances cellulose, hemicellulose and lignin are distributed. These substances are all of polymeric nature, and their relative occurence depends on the kind of wood.

2.1.1 Cellulose

Cellulose is the most important substance in the fibre wall, and its content in wood is about 40%. It is a linear polymer consisting of about 10 000 glucose monomers. The cellulose chains are arranged in bundles into fibrils with alternating crystalline and amorphous regions. Interaction between fibres and water principally take place in the amorphous regions and on the surfaces of the crystals. Due to its high stiffness and its fibril structure, the cellulose acts as reinforcement in the wood fibre.

2.1.2 Hemicellulose

Wood contains approximately 30% hemicellulose. Like cellulose, hemicellulose is a polysaccharide, but it consists of various kinds of monosaccharides. The hemicellulose polymers have, unlike the cellulose ones, often small side branches, and they are arranged into a principally amorphous structure. The function of the hemicellulose in the wood cell is probably to introduce flexibility and also to work as a binder between cellulose and lignin. In paper the hemicellulose contributes to the fibre bondings, and it is therefore very important to paper strength. Due to its amorphous structure, hemicellulose more easily absorbs water and reacts with process chemicals than cellulose, hence being broken down to some extent during the pulp production.

2.1.3 Lignin

The lignin content in wood varies from about 20% in hardwood to around 30% in softwood. Lignin is built up by aromatic carbohydrates which form a complicated structure that varies between different kinds of wood and the parts of the fibre where the lignin occcurs. Lignin is responsible for the binding of the fibres in the wood, and it mainly occurs in the fibre wall. It has a principally amorphous structure and is less hydrophilic than cellulose. The making of chemical pulp is based on different methods to make the lignin water soluble, which call for modification and partial breakdown of its chemical structure. The wood fibres can be separated when the main part of the lignin in the outer layer of the fibre wall is dissolved. Bleaching of the pulp dissolves and breaks down the rest of the lignin in other parts of the fibre wall. A problem with these chemical processes is to avoid breakdown of cellulose.

2.2 Added substances

In order to improve the quality of the paper, different substances are added to the stock or the paper in various amounts. Most of these substances are added to improve the optical properties of the paper, for instance colour and brightness, but these may also have an effect on the mechanical properties due to their structure and chemistry. The additives that are treated below are of particular importance to the optical properties of the paper. Others are added in order to facilitate the paper making, which is the case for the hydrophobic substances that are added to the stock in order to prevent the cellulose from absorbing water. Some substances, for example those used in paper coatings or for surface sizing of the paper, are added after or during the paper production. Coating is made in order to make the paper surface smoother and improve its brightness and printability. The coating principally consists of a polymer to which pigments, the functional part of the coating, have been added. The surface sizing, which is made by applying starch in the size press of the paper machine, makes the fibres in the surface layer become more strongly bound, which is important especially for paper used for printing.

2.2.1 Dyes

Addition of dyes is made in order to change the spectral distribution of the light reflected from the paper. The dyes used today are organic molecules with different chemical structures and side groups. The dyes absorb in certain wavelength bands, thereby determining the wavelengths of the light reflected from the paper. The shape of the absorption band determines the brightness and the purity of the colour. The dye molecules might also lose some of the absorbed energy in form of fluorescence light of certain wavelengths, which also affects the colour appearance of the paper. It is important that the dyes have high substantivity for paper fibres, which means that their ability to adsorb onto the fibres from an aqueous medium is good. Their affinity, the ability to bind to the fibres, must also be good. This is best carried out by the group of dyes called direct dyes, and especially by the cationic direct dyes, which also have high bleedfastness and good performance when applied to different pulp types. Other kinds of dyes are acid dyes, basic dyes and sulphur dyes. Dyes are principally applied to the paper by addition to the stock, but many different techniques exist.

Because of the limited interest of non-fluorescent dyes for this project, no deeper look is taken into the subject. An exhaustive treatment is given by Murray [1], to which the interested reader is directed.

2.2.2 Fluorescent whitening agents

Fluorescent whitening agents (FWAs), also called optical brightening agents (OBAs) or optical brighteners, are used to decrease the natural yellowness of the pulp. Today the use of FWAs is spread over a wide range of different paper products such as office paper, coated paper [2] and coated board. The FWAs absorb UV light and emit fluorescence light in the blue wavelength region, compensating for the absorption of the coloured substances in the pulp.

The FWAs were discovered and brought into the paper industry in the 1930s, when Swiss and German chemists were searching for a substance with high adsorption to the fibre, and with high absorption of UV light, that could prevent the UV light from reaching the fibres and induce yellowing of the paper. They found that stilbene derivatives had suitable absorption bands, but when these were applied and tested with UV light it was found that the paper became even whiter

due to fluorescence in the blue region. Although the intention to protect the paper from yellowing was not realised, it was later shown that FWAs can restore the whiteness if such yellowing has taken place [3].

In the paper industry the most commonly used FWAs are the diaminostilbene derivatives, in particular diacyl, diacyl sulfamide and triazinyl [4]. Stilbene based FWAs account for about 80% of commercially available brighteners [1].

When applying FWAs to paper, which is made through the stock, in the size press or by coating, the fact that they are self-reactive with cellulose makes the contact times very short before a uniform distribution takes place. Because of their comparatively small molecular size, FWAs can be absorbed by cellulose through the small pores created by swelling in the amorphous regions [5]. The mobility of the FWA molecule within the fibre walls enables it to diffuse through the wall structure and become fixed through hydrogen bonding. It has been noticed that the fluorescence efficiency of the FWA molecules is greater when they are attached to cellulose or any other carrier, e.g. carboxymethylcellulose (CMC), melamine or polyvinylalcohol, rather than simply in an aqueous solution [6]. Due to the fact that most FWAs used in the paper industry are anionic they tend to agglomerate when reacted with cationic additives, and this results in quenching of the fluorescence efficiency [4]. The affinity for cellulose, as well as solubility and substantivity, is also affected by the different groups bonded to the FWA substrate [1].

Due to raised environmental demands, efforts are made to limit the use of FWAs in the long run, but this process takes time and the advantages of the FWAs are still outweighing the disadvantages.

2.2.3 Fillers

Fillers are used in paper in order to either improve optical and printing properties of the paper, or simply reduce the production cost by replacing some of the raw material. Examples of the first kind are titanium dioxide, calcined clay, urea, formaldehyde, synthetic alumino-silicates and precipitated silica. These speciality fillers often have carefully controlled particle size distributions, high brightness and special attributes as high refraction index, low density or pore-rich aggregated particles. General purpose fillers, which can be related to the second category, are for example kaolin, chalk, limestone and talc. The particle size distribution of these fillers substantially falls within the range 10-0.5 μm [7].

The filler content in paper varies in a wide range depending on the type of paper and its field of use. Small quantities of fillers, up to 3%, are sometimes added in newsprint production in order to improve optical and printing properties. Office and journal paper may contain as much as 30% fillers, principally intended to reduce the cost. Considering coated papers, fillers are not used in the base paper when used in the coating, but fillers however enter in the base paper via the waste pulp.

Fillers have, as mentioned, a positive effect on the optical properties of paper, which will be discussed in section 3.3.4, but generally they also influence the strength of the paper in a negative way. The addition of fillers will result in a disruption of the cellulose fibre network. This will have indirect, positive effects on the light scattering, but it will also result in an overall decreased paper strength due to less fibre-to-fibre bonds. This problem will be discussed further in coming sections, since it is important also to the use of recycled fibre.

3   Optical properties of paper and substances in paper

3.1   The paper structure and its interaction with light

The porous paper structure principally consists of an air-filled fibre network to which added pigments such as fillers are bound. The light reflected from a paper is perceived as a diffuse reflection from the surface, but in fact there are a number of optical phenomena that occur: reflection, refraction, diffraction and absorption. These are in turn related to two main groups of processes when describing the light propagation in paper: scattering, to which not only diffraction but also reflection and refraction are related, and absorption.

Scattering or reflection occurs at interfaces between substances with differences in refractive index, i.e. at surfaces of fibres and particles in the superficial and inner regions of the paper. At the interfaces between air and cellulose refraction of the light can take place. Some of the light is absorbed by substances in the structure, and this can also give rise to fluorescence. Diffraction occurs when the light reaches particles or pores of sizes smaller than or of the same magnitude as the wavelength, but it decreases when the particle size gets smaller than half the wavelength. If the particle size is much smaller than the wavelength, Rayleigh scattering can take place. However, this is very weak compared with the light scattering that can be related to reflection and refraction.

The light that is not absorbed finally leaves the paper structure after a number of scatterings, reflections and refractions. Some of it returns to the surface where it is scattered in different directions, while the rest is transmitted through the back of the paper sheet. Due to the complexity of the structure, the light propagation through the paper may be thought of as a random chain of the processes described [8].

3.2   Defined optical properties of paper

The optical properties of the paper are very important since they principally determine the visual perception of the paper. Basic properties such as light scattering and absorption coefficients can be related to more easily handled properties such as brightness and opacity, which can be used to describe the appearance of the paper. Other properties, such as colour and Y-value, are adapted to the sensitivity of the eye. Methods for measurement of these properties have been standardised with respect to conditions regarding illumination and detection.

3.2.1 Light scattering and absorption coefficients

The two main groups of processes describing the propagation of light in paper, scattering and absorption, can be described by the scattering and absorption coefficients. They are both important parameters in the Kubelka-Munk equations, which describe the reflection of light from thin layers following diffuse illumination [9, 10]. As will be discussed later, a few important paper properties can be derived from these equations.

The absorption coefficient, denoted k and measured in m^2/kg, is a measure of the amount of light that is absorbed in the paper per basis weight unit. Generally speaking it is affected by bleaching, cooking and other pulping processes.

The scattering coefficient, denoted s and also measured in m^2/kg, is a measure of the presence of free surfaces in the paper structure, where scattering can occur. It is in general influenced by processes such as beating, pressing and calendering but also by addition of fillers. The product of the scattering coefficient and the basis weight is called the scattering power, which is a very important property of printing paper and a measure of the ability of the paper to hide print on the back side.

3.2.2 Reflectance and gloss

The reflectance, denoted R, is a wide spread property known from Fresnel's equations which in the special case of normal reflection yields

$$R = \left(\frac{n - n_0}{n + n_0}\right)^2 \tag{3.1}$$

where n and n_0 are the refraction indices of the material and air, respectively. However, when discussing paper properties, the reflectance is not as easily described as in the case of plane surfaces, due to the porous structure and the rough surface. As mentioned before, light is also scattered at the surface, and some of the light that is transmitted into the bulk structure can return to the surface after a number of scatterings in the inner regions. Reflectance therefore has a somewhat different meaning in paper optics.

A special reflectance property is the gloss, which is a measure of how much light that is scattered into a certain direction. It is often measured at the same angle of reflection as the incident one, but also at other angles. In order to improve the looks of the surface many paper grades have a surface finish that gives the paper certain gloss properties.

3.2.3 Reflectivity

The reflectivity of a paper, denoted R_∞, is defined as the reflectance of a thick pile of sheets, so thick that an added sheet does not influence the measured value. From the Kubelka-Munk equations, which describe light reflection from thin layers, the reflectivity can be expressed in terms of the absorption and scattering coefficients [9]:

$$\frac{k}{s} = \frac{(1 - R_\infty)^2}{2R_\infty} \tag{3.2}$$

The reflectivity is consequently a material constant that only depends on the ratio between the absorption and scattering coefficients.

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3.2.4 Opacity

The opacity is, as the name implies, a measure of how opaque, untransparent, the paper is. Like the reflectivity it can be related to the Kubelka-Munk equations and the absorption and scattering coefficients [9]:

$$Opacity \, / \, \% = 100 \cdot \frac{R_0}{R_\infty} \qquad (3.3)$$

where R_0 denotes the reflectance from a single sheet when measured with a black, nonreflecting background. Unlike the reflectivity R_∞, the reflectance R_0 is dependent on the basis weight of the paper and is thus not a material constant. From this it is easily understood that the opacity increases with increasing basis weight. Reflectance and reflectivity are conventionally measured with the same filter (with a transmission maximum at 557 nm) as used when measuring the Y-value (see section 3.2.6), and the opacity is obtained according to equation (3.3).

3.2.5 Colour

In 1852 Grassman proved that the colour perceived by the eye can be created by mixing three primary colours in certain proportions, provided that the third colour cannot be obtained by mixing the two others in any proportions [9, 10]. Young had earlier stated that three colours are enough for the eye to register to let all colours be perceived. In 1931 an international colorimetric standard, based on this theory, was made up. The standard is based on three spectral colour transfer functions, $x(\lambda)$, $y(\lambda)$ and $z(\lambda)$, which are based on the visual perception of light of different wavelengths and representing three virtual colours. Since the functions have a physiological and psychological origin they can not be described by a formula, but they are empirically determined for each nm in the visual part of the spectrum. The function $y(\lambda)$ is adapted to the spectral sensitivity of the eye, and its maximum value as well as its integrated area are normalised. The two other functions, $x(\lambda)$ and $z(\lambda)$, are fitted so that their integrated areas are of the same size as the one of $y(\lambda)$, which means that the three colours have equal contribution to a white mixture (the neutral point).

The colour of the paper can be described by the so called tristimulus values of the colour, which state the proportions to which the three virtual colours contribute to the colour. They are obtained by integrating the transfer functions, weighted with the spectral reflectance $R(\lambda)$ and the spectral energy distribution of the light $S(\lambda)$, over the whole wavelength region, 360-770 nm [9]:

$$X = k \sum_{360}^{770} x(\lambda) S(\lambda) R(\lambda) \Delta\lambda \qquad (3.4)$$

$$Y = k \sum_{360}^{770} y(\lambda) S(\lambda) R(\lambda) \Delta\lambda \qquad (3.5)$$

$$Z = k \sum_{360}^{770} z(\lambda) S(\lambda) R(\lambda) \Delta\lambda \qquad (3.6)$$

with the normalisation factor k defined as

$$k = \frac{100}{\sum\limits_{360}^{770} y(\lambda)S(\lambda)\Delta\lambda}$$

(3.7)

The tristimulus values are most often represented in relative values, the so called chromaticity coordinates:

$$x = \frac{X}{X + Y + Z}$$

(3.8)

$$y = \frac{Y}{X + Y + Z}$$

(3.9)

The chromaticity coordinates are a measure of the colour content of the paper, and together with the Y-value, representing the lightness, they give a distinct description of the colour.

3.2.6 Y-value

The Y-value, which is one of the three tristimulus values described above, is often used as a concise value of the reflectivity of a paper since it is adapted to the sensitivity of the human eye. The colour transfer function $y(\lambda)$ has its maximum at 557 nm, and when measuring the Y-value a filter with a transmission given by $y(\lambda)$ can be used together with a reflectance meter. It can also be obtained with a spectrophotometer by measuring $R(\lambda)$ and using equation (3.5).

3.2.7 Brightness

The natural colour of paper and pulp belongs to the yellow/red part of the spectrum. In order to be able to measure the effect of bleaching more sensibly, measurements of the reflectance are performed in the blue region where bleaching results in more distinct changes in reflectance. Measurements are made with a reflectance meter and a so called R_{457}-filter, which transmits light in the region 400-500 nm with a peak transmittance at 457 nm. The obtained reflectance value is denoted brightness (given in %). The brightness can also be obtained by measuring $R(\lambda)$ with a spectrophotometer and using equation (3.5) with the transfer function of the R_{457}-filter instead of $y(\lambda)$.

3.3   Optical properties of substances in paper

The optical properties of paper and pulp are not only due to the structure of the fibre network, but also to the incorporated natural and added substances in terms of absorption, fluorescence and scattering. Because of the varying content of these substances between different kinds of pulp the optical properties of the paper also depend on the pulp composition used in the paper production. This will be touched upon in chapter 4.

As for the fluorescence from substances in paper, the intensity of the fluorescence light principally depends on the concentration of the substance, its probability of absorbing the excitation light and its fluorescence (quantum) yield. The surrounding environment of the excited molecule is very important to the probability of absorption and to the fluorescence yield. Absorption of fluorescence

light by surrounding material, or collisions with neighbouring molecules, can result in a lowering of the detected fluorescence from a substance. Further, fluorescence light has a certain probability of being reabsorbed by the same substance, which leads to so called self-absorption and a decrease in the detected fluorescence intensity.

3.3.1 Cellulose

As mentioned in section 2.1.1 cellulose plays a great role as the fundamental ingredient in the fibre. It is thus natural to believe that the optical properties of the paper, at least to some extent, depend on cellulose. This dependence is essentially due to the structure built by the cellulose molecules, in terms of its enabling substances to be bound to it and the light to proceed through it. Cellulose has a refractive index of about 1.53, which leads to the occurance of scattering at the interfaces between cellulose and air.

Pure cellulose absorbs ultraviolet light with an absorption maximum at 265 nm [11]. The origin of the absorption has been assigned to the glycosidic bond of the cellulose molecule [12], but also to unsaturated or aromatic groups produced during isolation and purification of the cellulose. Another explanation of the absorption might be that absorption centres are formed by interaction between cellulose chains in the solid state [13].

Generally fluorescence can be detected from cellulose, but there is no easily explained reason for this [14]. Examples can also be found in [11], where highly purified cellulose samples of different origins (cellulose from wood, algae and bacteria) were excited with ultraviolet light of 320 nm, resulting in a fluorescence peak around 420 nm for all samples. It was suggested that the fluorescence might be due to emission centres generated during the purification and isolation processes or to inorganic impurities. Although residuals of lignin, which is highly fluorescent, could be excluded as the principal reason because of the non-lignified bacterial and algal cellulose, the intensities of the luminescence were of the same magnitude as those from samples of mechanical pulp, which contains a lot of lignin. Despite this, the fluorescence in unbleached paper not containing FWAs is dominated by lignin, which has an ability of absorbing a lot of the possible fluorescence light from cellulose.

3.3.2 Lignin

Lignin is considered being the main origin of the natural fluorescence in paper [3, 15, 16], and it is also responsible for the yellowness of paper due to its high absorption of blue light and UV light. The absorption of UV light also results in decomposition of the lignin molecules, which increases the absorption in the blue region and hence gives rise to further yellowing. Due to the variety of forms that its complex structure may appear in, the fluorescence spectrum of lignin may show variations, and the lignin molecule is also easily modified by chemical reactions during the pulp production. The delignification process, i.e. the dissolving of lignin from the wood fibre, can create fluorescent products from lignin that are left in the pulp and thus appear in the paper [3, 17]. In order to remove residual lignin, bleaching of the pulp is performed, which results in a decrease in the absorption coefficient and thus an increased reflectivity of the paper (see section 3.2.3).

Because of its high absorption of ultraviolet and blue light lignin exhibits its largest fluorescence, which is emitted in the green/yellow region, when excited by light of these wavelengths. The fluorescence spectrum of lignin following excitation with UV light has been thoroughly studied [15, 18, 19, 20]. One type of lignin studied emitted its maximum fluorescence intensity around 520 nm, with a full width at half maximum (FWHM) of about 160 nm, when excitation was made at 295 nm [15]. It was also found that the fluorescence decays with at least two different lifetimes.

At high lignin concentrations self-absorption can occur, particularily when excitation is made with UV light: blue fluorescence light is reabsorbed by other lignin molecules, which results in lower fluorescence intensities than the ones expected from those concentrations [15, 21]. When excitation is made with light of longer wavelengths, the fluorescence from lignin dominates over that from other natural substances in the paper and also over the fluorescence from added substances such as FWAs.

3.3.3 Fluorescent whitening agents

The optical behaviour of the FWA depends on its chemical constitution and surrounding, as described in section 2.2.2. An important measure of the fluorescence efficiency of an FWA is the quantum yield, which is defined as the part of FWA molecules that, once excited, emit fluorescence light instead of losing their energy in other ways, e.g. through vibrational relaxations. Depending on electron withdrawing and donating groups but also on the substrate of the FWA, different values of the quantum yield and different wavelength ranges of the fluorescence light are valid [1]. Generally electron withdrawing groups decrease the fluorescence, while donating groups increase it, but the substrate makes it not that simple.

The fluorescence of the FWA can be quenched in different ways, as mentioned in section 2.2.2. The agglomeration of FWAs when brought together with cationic additives results in quenching due to the fact that the agglomerates are less effective in absorbing UV light [4]. Another source of quenching is the absorption of UV light from other substances. Because of the strong UV absorption of lignin, FWAs are not generally added to mechanical pulps. For the same reason, as will be discussed in section 3.3.4, they are neither used in papers filled with titanium dioxide.

The FWAs are gradually decomposed or broken down when exposed to intense UV light. Because of the following decrease in fluorescence, the paper then starts to look a bit yellow. This phenomenon should not be confused with the yellowing of paper containing lignin, which is due to an increase in the absorption of blue light following oxidation of coloured groups in lignin [10].

The effects following addition of FWAs to paper have been investigated thoroughly over the years [4, 22, 23, 24]. Most studies have been made using a reflectometer with a removable UV filter [25] or with a spectrophotometer [23]. It has been observed that the increase in brightness due to fluorescence from FWAs declines with increasing FWA content in the paper. In some case a decrease in fluorescence, and even yellowing of the paper, has been observed when further addition of FWAs is made beyond a certain level [23]. Like in the case of lignin this has been assigned to self-absorption, but the effect is more obvious for lignin.

The fluorescence from FWAs is totally dominating over the fluorescence from other substances in paper when excitation is made with UV light [15]. For a typical FWA of stilbene-type (in solution) the maximum fluorescence intensity has been detected around 430 nm with a FWHM of about 60 nm, following excitation at 295 nm. The fluorescence decay of the same substance has also been studied, giving a single lifetime of 1.2 ns. FWAs exhibit almost no fluorescence at wavelengths longer than 500 nm.

3.3.4 Fillers

The most important factors affecting the optical properties of paper containing fillers are the refractive index of the filler, the specific surface of the sheet structure, the interaction between the filler particles and the fibres, the pore structure and the light absorption of the filler particles.

In order to get good light scattering the refractive index of the filler should be high. Most of the fillers used have refractive indices slightly higher than that of cellulose (see table 3.1 below). Kaolin and calcium carbonate, for example, both have a refractive index of 1.57. There are also fillers with extreme refractive indices. Titanium dioxide, with a refractive index of about 2.6, is mostly used. Because of their high scattering coefficients, these fillers can increase the brightness and the opacity of the paper.

The light scattering is also dependent of the particle size, which means that it depends on the specific surface of the filler (see table 3.1), and on the wavelength of the illuminant light. The scattering as a function of particle size passes through a maximum corresponding to an optimum particle size [7]. A decrease in scattering appears when the particles are smaller than half the wavelength of illumination. This means that the optimum size is dependent on the wavelength, but it also depends on the particle shape and the refractive index of the filler. It lies in the range 0.4-0.8 μm for fillers like kaolin and calcium carbonate and around 0.2 μm for titanium dioxide [10]. Increasing the wavelength of illumination results in a decrease of the light scattering coefficient and an increase in optimum particle size.

Filler	Refractive index	Specific surface/ m^2kg^{-1}	Light scattering coefficient/ m^2kg^{-1}	Light absorption coefficient/ m^2kg^{-1}
Clay (kaolin)	1.57	8	150	2.5-3.5
Calcium carbonate	1.57		130-150	
Marble	1.57			0.4-0.6
Calcined clay	1.60	17	340	1.2-2.0
Precipitated calcium carbonate (PCC)	1.60	6-20		
Titanium dioxide	2.6		1000	

Table 3.1 Refractive indices and some other optically related values for some different fillers [9, 10]. The light scattering coefficients are given at 450 nm for a typical uncalendered fine paper furnished with a filler content of about 20 wt%. The light absorption coefficients are given at the same wavelength.

For fillers with refractive indices close to that of cellulose the air interfaces, such as those formed by pores, are the important ones for scattering [10]. Small filler particles that are well distributed on the fibre surfaces give rise to high scattering. However, the fibres themselves contribute to the scattering to a certain extent depending on their free surface, i.e. the part of the fibre surface that is not taking part in bonds. The addition of filler particles prevents bonding so that the free interior surface of the fibres becomes larger. A scattering dependence on size similar to that for particles is valid, i.e. there is an optimum pore size larger than half the wavelength of illumination. This explains much of the scattering power of low refractive index fillers.

The light-absorption of a filler is dependent on the bulk chemistry of the filler and on the presence of coloured impurities [10]. Natural organic materials and charge transfer complexes are usual sources of colour in natural mineral fillers, while synthetic fillers generally have very low light-absorption. As mentioned in section 3.3.3, the absorption of UV light is important when fillers are used in paper containing fluorescent whitening agents. Most fillers containing iron or organic contamination can reduce the efficiency of FWAs by about 20% at a filler content of 20% in the paper, compared with similar fillers with no contamination [7]. Titanium dioxide has a special position: it is in itself a very strong UV absorber, and a filler content of only 5% can be enough to reduce the FWA efficiency by 50%. This problem has limited the use of titanium dioxide as a filler in paper. When fillers are used together with bleached pulp their light absorption can dominate in the paper since bleached pulp has low light absorption [10].

Fillers have no apparent fluorescence themselves, but as mentioned impurities occuring in natural minerals can make these fluoresce. In measurements made on calcium carbonate from a natural source [15], fluorescence was detected in the same wavelength region as that from the FWA: the maximum intensity occured around 430 nm with a FWHM of about 50 nm following ultraviolet excitation. The fluorescence decayed with a single lifetime of about 0.8 ns. However the signal from the filler was strongly enhanced by scattering of the excitation light, resulting in fluorescence from a larger volume. This is though not likely to occur in paper containing lignin, which has high absorption of UV light. Using a measurement geometry less sensitive to scattering in the sample resulted in the intensity of the fluorescence from the FWA being about 400 times higher than that from the filler. On the other hand fillers are added in much larger quantities than FWAs, so their contribution to the fluorescence from paper may not be excluded.

4 Composition and properties of newsprint

4.1 Important newsprint properties

Newsprint is made from a few different pulp types which exhibit different optical and mechanical properties. The properties of the produced newsprint are ruled by production conditions as well as customer needs. In order to maintain stable production the paper must perform well in the paper machine, the winder and in particular in the printing machine. Demands on printability and optical properties must also be satisfied. Important properties are basis weight, colour, brightness, opacity, surface smoothness, et cetera.

The dominating basis weight of Swedish newsprint for domestic use is 45.0 g/m^2 (1991), but paper of basis weights 40.0, 42.5 and 48.8 g/m^2 as well as basis weights of over 50 g/m^2 (for foreign use) are also produced [26].

The optical properties are very important for newsprint and other paper grades used for printing. This is due to the fact that they, to a large extent, determine the human perception of the paper and the print. There are in turn a lot of factors, such as used pulp types and added substances, that determine the optical properties. In order to let a printing house use newsprint from different paper mills in the same printing without risking too large colour differences, a colour standard, News Shade 88, has been defined [10, 26]. Measurements of colour, brightness and opacity are therefore frequently made during production, and from the data decisions can be made whether addition of shading dyestuff or bleaching of the chemical pulp has to be changed or not. Bleaching will result in decreasing opacity because of decreasing scattering coefficient (see section 3.2), but this can be compensated for either by increasing the basis weight or by adding fillers. Except for the standard newsprint, special newsprint grades are also made to meet specific customer needs.

High surface smoothness results in good printing performance and low ink need. A lot of different factors such as pulp quality, forming, drying and calendering affect the smoothness of the paper.

4.2 Different pulp types used in newsprint production

4.2.1 Mechanical pulps

Mechanical pulp is the basic component in newsprint, and in Scandinavia it is essentially made from spruce. Because of its high opacity and fast absorption of ink, the mechanical pulp is very suitable for printing. The mechanical pulp used for newsprint production is of two kinds depending on the process chosen for the pulp production: stone groundwood (SGW) and thermomechanical pulp (TMP). The wood is broken up mechanically, and by using heat and moisture the fibres are layed free in a way that bonds can be formed between them in the paper.

Several investigations concerning the fluorescence from mechanical pulps have been performed [11, 15, 16, 17, 27]. Because of the large content of lignin, up to 30%, in mechanical pulps their fluorescence spectrum and decay lifetimes are similar to those of lignin.

The *stone groundwood*, which is of limited use in Sweden, gives high opacity of the paper. Because of the mechanical treatment the SGW contains a lot of fine material and fragments from damaged fibres, which improves the light scattering. On the other hand this also decreases the strength, and it is therefore necessary to use reinforcement fibre in form of chemical pulp. Further it is difficult to purify the SGW, and difficulties also occur in controlling the process to a get good and even quality.

The *thermomechanical pulp* is the dominating pulp in Swedish newsprint mills. Its quality has been improved through process development in order to satisfy high demands on strength and purity. Unlike the SGW it has a larger content of undamaged fibres due to the lighter treatment and consequently a higher strength. Less reinforcement pulp is therefore needed when using TMP instead of SGW, and in some cases the reinforcement pulp can be totally excluded. Normally, due to the smaller content of fines, the TMP has less light scattering ability than SGW, but this is to some extent compensated for because of the addition of less reinforcement pulp, which has an even worse light scattering ability.

4.2.2 Chemical pulps

Chemical pulps are also used in newsprint production, however to a smaller extent. As mentioned before their main purpose is to work as reinforcement in order to increase the strength of the paper. Of the existing pulps, the chemical pulps are the ones that give the highest paper strength. During the production of chemical pulp, which is performed by cooking wood chips in water together with certain inorganic compounds, the fibres are layed free by dissolving the lignin that holds them together, and the fibres are therefore almost undamaged. In order to remove more lignin and satisfy demands on colour and brightness, bleaching of the pulp is performed. During both cooking and bleaching the strength of each single fibre is somewhat decreased since some of the cellulose and hemicellulose in the fibres is also broken down.

Because of the careful defibration the mean fibre length is larger for chemical pulps than for mechanical pulps. By beating the pulp, which has to be made with all chemical pulps, different properties can be obtained. The beating results in increased paper strength overall, but in decreased scattering ability and air permeance due to a higher degree of bonding.

The chemical pulp is of two kinds depending on the cooking process used: sulphate pulp and sulphite pulp. For reinforcement of newsprint semibleached sulphate pulp is principally used.

4.2.3 Recovery pulp

Recovery pulp (RP), also denoted deinked pulp (DIP), consists of deinked fibres from recycled newsprint, journal paper and fine paper. The main advantages of using recycled fibre are less energy consumption and lower cost. Deinking of recycled fibre utilises 500 kWh per ton, which should be compared with the consumption of ca 2500 kWh per ton in TMP production [26].

Today up to 60% DIP is mixed into the stock in Swedish newsprint mills [26]. It is important that the pulp is deinked and bleached enough to satisfy the demands on paper brightness. Due to the lower strength of the recycled fibre, it is also important that it is purified enough not to increase the interruption frequency of the paper machine. The addition of recycled fibre to the stock also affects the demands on other components in the stock. For example further bleaching of the mechanical pulp might be necessary to maintain the brightness, and attention must also be paid to the impact on paper strength from the recycled fibre. The content of journal paper, which has a filler percentage of up to 30%, is important to the paper strength. Other influencing factors are the

deinking processes and, of course, the quality of the recycled paper. Less addition of chemical pulp following increased TMP quality, as well as the increasing amount of aged fibres in the recycled paper, might affect the quality of the recovery pulp. The content of chemical fibre in journal paper is today about 15-20% [28], but it might be lower depending on the strength of the mechanical pulp used.

Because of the use of recycled journal and fine paper in the DIP, fillers and fluorescent whitening agents are introduced in the newsprint. Swedish newsprint mills use recovery pulp with a content of approximately 30% journal paper, which results in a filler content of about 9% in the paper when using 50% DIP [26]. As mentioned in sections 3.3.4 and 2.2.3, the fillers increase the brightness and the opacity but decrease the strength of the paper. To lower the filler content in the recovery pulp during purification is both difficult and expensive. Addition of reinforcement fibre can compensate for the loss of strength, but it is not an economically good solution.

Thorough studies on the impact of recycled fibre on newsprint properties and printability have been performed by the Swedish Newsprint Research Centre (TFL) [26, 29]. It was above all found that the paper density at a certain surface roughness had a linear dependence on the DIP content, which was probably due to the filler content and the softer fibres of the recovery pulp. Neither formation nor strength were significantly affected, but at a constant calendering pressure the surface roughness and the air permeance decreased with increasing DIP content. Measurements of the optical properties showed that the Y-value decreased with increasing DIP content, though not preventing the optical demands from being satisfied. Regarding printing properties, which of course are very important when discussing the impact of recycled fibre on newsprint, tests showed no obvious effect for paper containing up to 50% DIP. It was shown that the ink need, the pigment penetration and the roughness of the printed surfaces were overall the same. However an increased oil penetration was noticed, resulting in increased print-through.

Due to the occurence of fillers and FWAs in the recovery pulp, it is reasonable to believe that its fluorescence properties are very similar to those of these substances. The largest fluorescence signal from newsprint made from recovery pulp is obtained in the blue region (maximum around 430 nm, FWHM=60 nm) following excitation with ultraviolet light (295 nm) [15]. Measurements made on copy paper also show similarities to the fluorescence pattern from FWAs and fillers. Newsprint made without recovery pulp does not exhibit this fluorescence. It can thus be concluded that, following ultraviolet excitation, the fluorescence from pulp and paper containing recycled fibre is not dominated by fluorescence from lignin, as in the case of mechanical pulp, but from FWAs and fillers in recycled fine paper. This important fact will be the basis of the idea of measuring the distribution of recycled fibre using fluorescence, which will be discussed in detail in chapter 5.

5 Needs and possibilities of monitoring the distribution of substances during newsprint production

Following the technological development in the paper industy during the last decades and the gradually heavier quality demands, the needs of controlling the production process have grown. The possibilty of making immediate changes in stock composition or addition of for example dyes or fillers has given rise to development of equipment for on-line inspection of different paper properties. Today for instance basis weight, formation and colour can be monitored during production. Since most paper properties are directly dependent on the chemical composition of the paper, techniques for determining the distribution of different substances and components during production, and thereby getting accurate indications of what changes are to be made, would be very important. Methods and equipment for such inspection have however not been available.

5.1 Needs of on-line monitoring of the distribution of different substances in newsprint

The needs of on-line monitoring of the distribution of substances have become even more important following the growing use of recycled paper in the paper industry. The consequences following the use of recycled fibre in newsprint production were discussed in section 4.2.3. It was concluded that any large impact should not be feared for contents of up to 50% recycled fibre in the stock. However, the results of the studies performed are not clear overall, and there might also be local variations depending on the retention. Demands from customers on a guaranteed minimum content of recycled fibres, as well as an eagerness from the producers to use as much recovery pulp as possible due to energy reasons, will most probably result in a successive raising of the content of recycled fibre in newsprint. Because of the problems that might then appear, on-line monitoring would be a great step forward for the possibilities of maintaining the quality of the paper.

Not only the distribution of recycled fibre, but also that of other substances, is of course important to monitor since the properties of the paper to a large extent depend on the concise effect from all paper components. The lignin distibution, for instance, is on the whole a measure of the homogeneity of the paper, but it is also important to study the bleaching efficiency by measuring the lignin concentration of the chemical pulp. In paper made from mechanical pulp and bleached chemical pulp, the lignin distribution can be related to the distribution of fibres from the mechanical pulp.

5.2 Fluorescence as a tool for identification of substances and their concentrations

As was discussed in section 3.3, many of the substances in paper emit fluorescence light after having absorbed light of certain wavelengths. The fluorescence light is characteristic for each substance in ways of having certain spectral distributions and decays of certain lifetimes. Since its intensity depends on the concentration of the fluorescent substance, fluorescence can be used not

only for detection but also for concentration measurements of different substances. Using optical methods for these kinds of inspection have further advantages because of the possibility of performing fast and well-resolved measurements without any physical contact with the measured sample. High-speed methods are desirable for measurements on running paper webs. For instance, paper machines for newsprint production have a typical web speed of 20 m/s.

Fluorescence measurements of different substances have been applied in a wide range of fields, so also in the paper industry. As mentioned in section 3.3, the fluorescence emission from paper substances and pulps has been investigated thoroughly. Some of the investigations have resulted in useful methods for industrial inspection, for instance possibilities of determining the lignin concentration in pulps and pulping liquors [21, 30, 31]. These measurements of lignin have all been performed using excitation with UV light, which might cause difficulties because of the self-absorption as mentioned in section 3.3.2. Possibilities of using laser-induced fluorescence for imaging of paper surfaces have also been investigated [32].

Investigations of the possibilities of using fluorescence for monitoring of newsprint production have been initiated in a project involving the Swedish Newsprint Research Centre (TFL) and the Division of Atomic Physics. Not only the fluorescence properties of newsprint and different substances and components in newsprint have been investigated [15], but also basic phenomena regarding the interaction between light and paper [8]. This is important for the development of optical equipment for different kinds of measurements on paper. From the fluorescence measurements [15] it was concluded that the fluorescence from newsprint is dominated by lignin and, in newsprint containing recycled fibre, by recycled fine paper. Further these two components can be identified by both their temporal and spectral behaviour. Following excitation with ultaviolet light the dominating fluorescence from newsprint containing recycled fibre was related to recycled fine paper, and this fluorescence showed large similarities to that of a fluorescent whitening agent. Excitation with visible light on the other hand resulted in a dominating fluorescence originating from lignin. This identification of lignin and recycled material has opened up possibilities of doing individual measurements of distribution and concentration for each substance. The fact that lignin can be studied using excitation with visible light instead of ultraviolet is in itself important: the problem of notable self-absorption, which is due to the small mean free path for absorption at short wavelengths, can be avoided by instead using visible excitation light and detecting the fluorescence light close to the wavelength where the mean free path for absorption has its maximum.

From the experience described above, a portable fluorescence meter for on-line measurements of the lignin distribution has been constructed [33] at the Division of Atomic Physics. Excitation is made with a HeNe-laser at 632.8 nm, and the fluorescence light is detected around 700 nm with a FWHM of 40 nm. The characteristics of the equipment have been tested [33, 34], and measurements on paper strips from newsprint mills have also been performed, revealing some interesting properties of the paper related to production conditions.

In this project, a similar fluorescence meter for on-line monitoring of recycled fibre has been constructed and tested. The development will be described in chapter 6.

6   Development of equipment

6.1   Optical design considerations

The experience from the fluorescence measurements in [15] has pointed at the possibility of using fluorescence detection in the blue region, following ultraviolet excitation, for measurements of the distribution of recycled fibre.

Considering the optical design of the equipment, the excitation light should be focused to a small volume in the paper in order to get good spatial resolution. Since the fluorescence light should be collected from the same volume, it is preferable to use the same lens for focusing the excitation light as for collecting the fluorescence light. The fluorescence and excitation light must therefore be guided partly through the same optical system, which demands that spectral separation easily can be made by means of filters and dichroic mirrors. This is important for the choice of light source and filters. Further, the fluorescence from other substances in the paper, in the first place lignin, can contribute to the signal, especially when the content of recycled fibre is low. By choosing an appropriate wavelength interval for detection of fluorescence light, the influence of other substances may be reduced.

It has been found [15] that recycled fibre in newprint has its maximum fluorescence around 430 nm with a FWHM of 60 nm following excitation at 295 nm. Considering the demand on spectral separation of excitation and fluorescence light for this equipment, excitation around 300 nm and detection somewhere above 400 nm is a good fulfilment.

6.1.1 The light source

With respect to possibility of choosing wavelength interval and aspects of cost, size and efficiency, the most appropriate light source is a high pressure lamp. Since the ultraviolet region is desired in this project, a mercury lamp would be the best choice because of its high irradiance at these wavelengths. Considering the size of the arc, which should be small to satisfy the need of good optical quality of the system, and the needed output power to get an efficient excitation, a 100 W Hg lamp with an effective arc size of 0.25 mm × 0.25 mm is chosen. The lamp condenser produces a parallel beam of diameter 30 mm exiting the lamp housing.

In order to isolate the wanted wavelength region around 300 nm, the light source is supplied with a few accessories according to the drawing in figure 6.1. The light is first sent through a water filter with fused silica windows to pass the 250-950 nm range and absorb the infrared region. Despite the absorption, cooling is not needed as the output power does not exceed 100 W. A dichroic mirror, mounted in a beam turner, is then reflecting the 260-320 nm range at an incident angle of 45°, while the rest of the light is transmitted through the dichroic mirror and absorbed in the beam turner, which is supplied with cooling flanges. If further reduction of the wavelength range is needed, additional filters can be mounted at the light exit. A UV band pass filter is placed there to block the small amount of visible light that is reflected at the surface of the dichroic mirror.

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6.1.2 The optical system

The light is to be sent vertically to the paper surface and focused by an exit lens to excite the molecules in a certain volume in the paper. The fluorescence light can then be collected by the same lens and guided to a detector, as shown in figure 6.1.

By using a dichroic mirror reflecting the 260-320 nm range and transmitting longer wavelengths, the excitation light and the blue fluorescence light can be transmitted through the same system. The dichroic mirror is mounted at an angle of 45°, thereby reflecting the UV light downwards and letting the fluorescence light pass upwards. A plano-convex lens, which is mounted in a holder that can be translated for focus adjustment, collects the UV light to a spot on the paper surface and collects the light returned from the paper. Any reflected UV light is stopped by the dichroic mirror and reflected back to the lamp, while the fluorescence light proceeds through the mirror. A totally reflecting mirror mounted at the same angle as the dichroic mirror then directs the fluorescence light horizontally, and by means of a lens the light is collected onto the detector.

In front of the detector suitable filters are mounted in order to isolate the wavelength interval in which detection is to be made and to block any kind of background stray light, i.e. the small amount of UV-light that might be transmitted through the dichroic mirror, blue fluorescence light originating from the optical system and to a small extent light from the room entering through the lens in the bottom. From commercially available interference filters, two alternative filters with transmissiom maximum at 450 nm and FWHMs of 10 nm and 40 nm, respectively, are chosen (see the component list in section 6.2.2). Filters with a transmission maximum at for example 400 nm would be worse since the fluorescence from recycled fibre is weaker at 400 nm, and also a good separation of the excitation and fluorescence light would be somewhat more difficult to achieve at 400 nm. In addition one or more long-pass filters, with cut-off wavelengths of 400 nm and 420 nm, respectively, are chosen to prevent some of the stray light from reaching the detector.

6.1.3 The detection and signal registration system

The desire to perform on-line high speed measurements call for use of a fast detector. The detector should also have high sensitivity in the blue region where detection is to be made. To satisfy these needs, a photomultiplier tube (PMT) with high sensitivity for blue light is chosen. The signal from the PMT is amplified by the socket assembly connected to it. Because of the large amount of outcoming data, a fast AD-converter connected to a computer is needed to register the fluorescence signal along the paper web.

6.2 The complete construction

The optical and electronic parts of the equipment, except for the light source, are placed in a closed box of size (length×width×height) 600mm × 300mm × 300 mm, according to the drawing in figure 6.1. A hole for the bottom lens, centered 65 mm from the short side, and a hole in the front side wall for the condensing lens assembly of the lamp are made. The top cover of the box can be opened for focus and mirror adjustments, filter replacements, et cetera. Controls and switches for the electronics are placed on the front panel, as well as a connector for the output signal, as described in sections 6.2.2 and 6.2.3.

Seen from above:
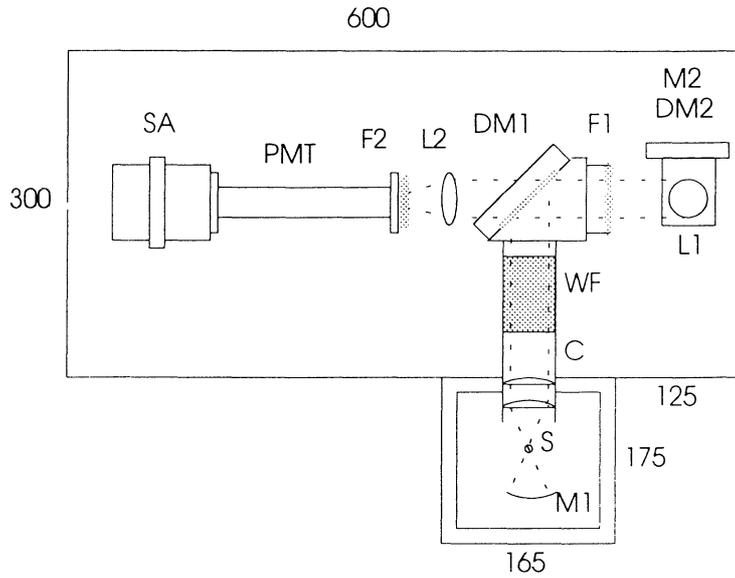
Seen sideface:
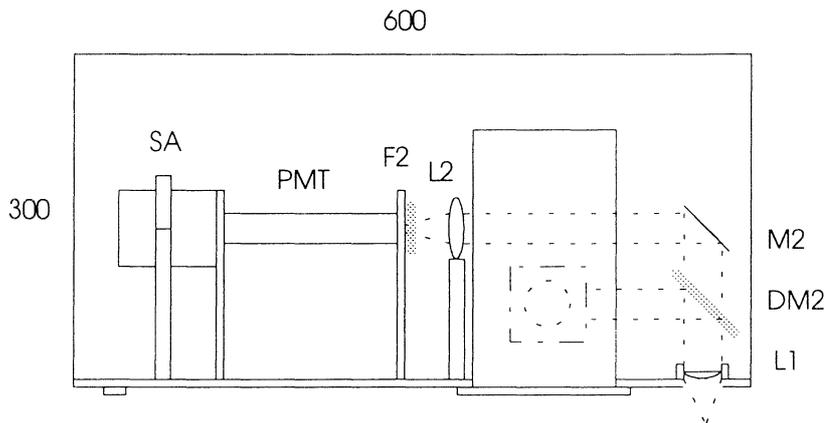
Fig. 6.1 Drawing of the optical design of the equipment, also showing exterior measures in mm.
Used component denotations:
S= Light source
C= Condenser, adjustable
WF= Water filter
M1= Back reflector (spherical), adjustable
M2= Flat mirror, adjustable
DM1= Dichroic mirror
DM2= Dichroic mirror, adjustable
F1= UV band pass filter
F2= Interference filter and long pass filter
L1= Plano-convex lens, adjustable
L2= Plano-convex lens
PMT= Photomultiplier tube
SA= PMT socket assembly

6.2.1 Specification of components used

The following optical and electronic components are used for the equipment:

Light source: Oriel 100 W Hg arc lamp 6281
Oriel lamp housing 66002
Oriel arc lamp power supply 68805

Condenser: Oriel F/1 two element fused silica condenser

Filters: Oriel water filter 61945; transmitting the range 250-950 nm, blocking IR
Oriel beam turning assembly 66245, with dichroic mirror 66217
    reflecting the range 260-320 nm
Melles Griot interference filter 03FIV004,
    transmitting at 450 nm with FWHM=10 nm
Melles Griot interference filter 03FIV028,
    transmitting at 450 nm with FWHM=40 nm
Schott UV band pass filter UG 11, transmitting the range 250-400 nm
    with peak at 330 nm
Schott long pass filter GG 400, cut-off wavelength at 400 nm
Schott long pass filter GG 420, cut-off wavelength at 420 nm

Filter holder: Oriel multiple filter holder 62020

Mirrors: Oriel dichroic mirror 66217
Melles Griot flat mirror 02MFG005 with kinematic mirror mount 07MMC506

Lenses: Melles Griot plano-convex synthetic fused silica lens 01LQF036,
    diameter 40.0 mm, focal length 50.0 mm (L1)
Melles Griot plano-convex glass lens 01LPX161,
    diameter 50.8 mm, focal length 88.9 mm (L2)

Light detector: Hamamatsu photomultiplier tube R268 with magnetic shielding
Hamamatsu socket assembly C1053 with a built-in amplifier
Hamamatsu modular high voltage power supply C1309-2

AD-converter: Datel PC-414A2, 12 bit resolution, bandwidth 1 MHz;
    complete with software PC-414SET

6.2.2 Electronics

The electronic arrangements are shown in figure 6.2 below. The voltage divider circuit of the PMT socket assembly is supplied with high voltage (-200 V to -1100 V) from the modular power supply, and a potentiometer (PMT h.v. control) on the front of the equipment box, see figure 6.3, is used to set the high voltage. A higher voltage setting results in a higher amplification of the PMT current created by the incoming photons. The amplifier in the socket assembly is supplied with ±15 V from a net adapter inside the box, which also supplies the modular power supply with +15 V. The recommended maximum output signal from the socket assembly is 10 V, which corresponds to an input signal current of 12.5 μA from the PMT. Above the maximum output signal level the amplification differs from the predicted linear one, which results in uncertainty of the incoming signal. From the socket assembly the output signal is led to a BNC connector on the front, where also a net switch and a fuse are placed.
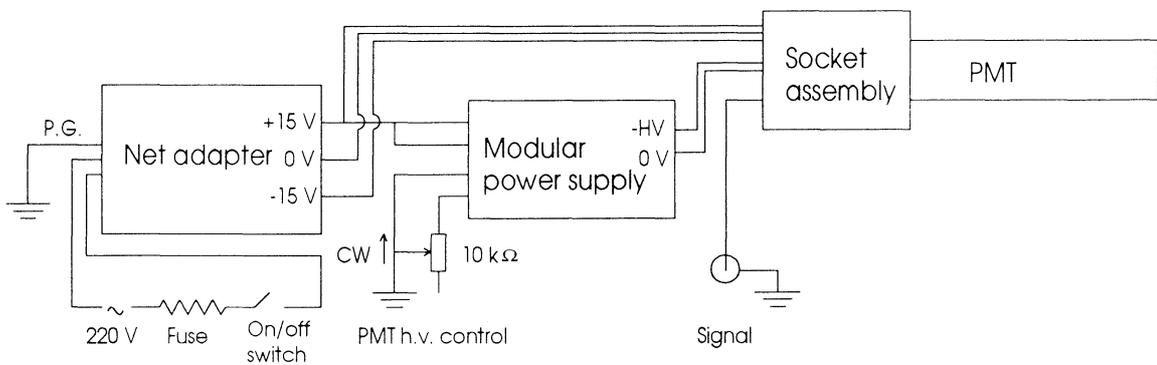

**Fig. 6.2** Arrangement of the electronics of the equipment.

6.2.3 Exterior design and operation of the equipment

The power supply, illustrated in figure 6.3 together with the rest of the equipment, supplies the lamp with a load dependent high voltage. The delivered power, which is shown on the meter display, can be changed by adjusting the output current with the knob (3). When the lamp start button (2) is pressed, a square wave voltage signal is sent to the lamp ignitor (8), which then produces high voltage pulses to start the lamp.

The lamp housing is equipped with a few knobs for positioning of the lamp (10, 11) and the back reflector (12-14). The fan (15) provides cooling of the lamp. Via the safety interlock switch (9) the power supply is automatically turned off in case of for example excessive temperature rises within the lamp housing.

The mains cord (16) is connected to the built-in net adapter of the equipment, which delivers voltage to the detector (see figure 6.2). A red lamp indicates that the power is switched on (19). The potentiometer (20), the PMT high voltage control, is used to set the high voltage that is delivered to the PMT socket assembly according to section 6.2.2. The control is graded from 0 to 10, where 0 corresponds to -200 V and 10 to -1100 V. Care must be taken in setting the high voltage so that the output signal voltage from the detector does not exceed 10 V; otherwise the correspondance between the input and output signals is lost, and there is a risk that the produced signal current in the PMT exceeds the maximum 0.1 mA, which can result in detector damage.

From the BNC connector (18) the output signal from the detector is led to the AD-converter, connected to a computer. The sampling conditions and the measurements are controlled via the installed software.
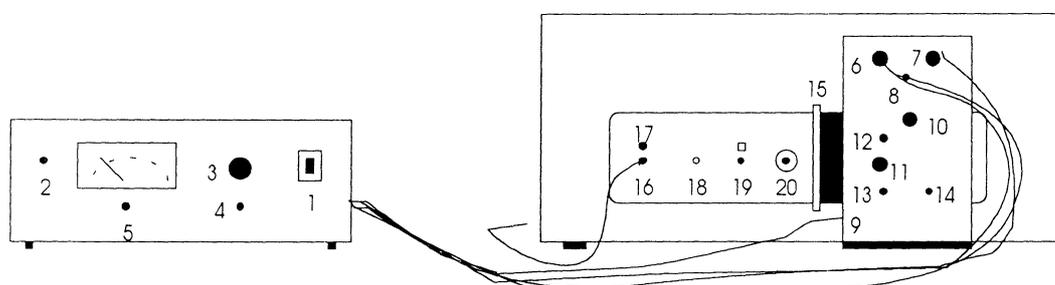
Power supply	Lamp	Equipment box
1 Power switch	6, 7 High voltage connectors	16 Net connector, 220 V AC
2 Lamp start button	8 Ignitor drive connector	17 Fuse
3 Output current/power adjustment knob	9 Safety interlock connector	18 PMT signal output
4 Current preadjust switch	10, 11 Lamp adjusters	19 PMT on/off switch
5 Meter display switch	12, 13, 14 Reflector adjusters	20 PMT high voltage control
	15 Fan	

Fig. 6.3 Exterior details of the equipment.

7 Testing and optimisation of the equipment

7.1 Beam adjustments

As the arc size of the Hg-lamp is 0.25 mm × 0.25 mm, it should be possible to focus the light to a spot just slightly larger than this size. This, however, demands that the back reflector of the lamp produces a good image of the arc and that no large distorsion of the beam occurs in the optical system.

In order to adjust the lamp to get a parallel beam and an arc imaging of good quality, the water filter and the beam turner are lifted off, and the light is focused by the condenser to form an image of the arc on a wall at a distance of a few meters. By means of the lamp adjusters the horizontal and vertical position of the lamp is adjusted so that the arc is positioned on the optical axis of the condenser. The reflector adjusters are then used to position the reflector, which is spherical, so that its distance from the arc equals its radius of curvature, which means that the images of the arc formed by light coming directly from the arc and light coming via the reflector, respectively, are of the same size and are overlapping in the same plane. After connecting the lamp to the rest of the equipment the condensor is adjusted so that parallel light leaves the beam turner. By means of an adjustable mirror holder the UV light reflected at the surface of the dichroic mirror (DM2) can be guided through the bottom lens. The upper mirror (M2) is adjusted so that the fluorescence light is sent through the lens (L2), symetrically around the optical axis, to be collected onto the photomultiplier tube. The bottom lens of the equipment is adjusted so that the light is focused to a spot on the paper surface.

However, the diameter of the focal spot turns out to be about 1.5 mm, which is considerably larger than the arc size. An investigation of the beam behaviour in the equipment has given reasons to believe that the origin of the spot enlargement is the optical system of the lamp, i.e. the back reflector or the condenser. Differences in the light intensity distribution between cross sections along the beam exiting the lamp can also be noticed. The optical quality of the beam might be improved by placing a spatial filter at the beam exit, thereby removing some of the stray light and finally getting a smaller spot size.

7.2 Measurement conditions

When doing measurements on paper it is important that the sample is moved while measuring, so that measurements are not made on the same spot. This is partly because of the uneven distribution of the fluorescent material, but also because of the fact that the fluorescence signal is decreased when measuring on the same spot due to induced changes in the FWA and lignin composition in the illuminated volume. In the measurements discussed in chapters 7 and 8, the paper samples were moved at a speed of 5 mm/s on a support of black painted aluminium. With the obtained spot size of approximately 1.5 mm the speed at which the samples are moved is sufficiently high not to induce any evident decrease in the measured signal. This is since the time of illumination of a spot of that size on the paper is 0.3 s, and during that time the signal from a certain spot is constant with three valid numbers.

7.3 Measurements for optimisation

The most important feature of the equipment should be its ability to give a high signal to background ratio (S/B-ratio) for paper containing recycled fibre. This means that signal changes more likely will be due to differences in the FWA concentration in the paper than to differences in the background light reaching the detector. It is also important, because of the strong lignin fluorescence, to get the signal response for FWAs as large as possible compared with that of lignin, i.e. maximise what will be called "the FWA/lignin-ratio". By choosing a certain filter setup, these features can be optimised.

Light from the room entering through the bottom lens can contribute to the signal. How much light that enters is dependent on the reflection and scattering properties of the measured sample and on its fluorescence. A measure of this contribution, also dependent on the filters used, at different PMT high voltages is needed.

Internal background light, emanating from the lamp and from fluorescence in the optics, can also effect the measured signal. As in the case of light from the room, the magnitude of this background is dependent on the filter setup.

Some, although a very small part, of the background derives from the PMT itself in form of the dark current. The magnitude of the dark current at different PMT high voltages should therefore be investigated.

The strength of the signal and the S/B-ratio is also dependent on the lamp power. A higher light intensity will hopefully increase the true fluorescence signal to a greater extent than the background contribution.

The change in signal following vertical displacement out of focus should be small in order to prevent paper wrinkles and vertical displacements of the paper web from having too much impact on the signal. This problem originates in the fact that a larger volume in the paper is excited when the light spot is out of focus, but all fluorescence light from this volume may not reach the detector.

Because of the UV absorption of the paper constituents the penetration depth of the UV-light is quite small. However, the influence of different support materials for measurements must be investigated.

Another interesting feature is the resolving power, which indicates to what limit small patterns of fluorescent material can be detected by the equipment.

The reproducibility of the equipment, which guarantees the absence of random influences on the signal, is important. It can be tested by measuring twice along the same track of a paper sample, and this was done after testing the equipment on paper samples with varying DIP content. The results of these measurements are included in chapter 8.

7.3.1 PMT dark current contribution

In these measurements the light source was turned off and the bottom hole of the box covered in order to prevent any kind of light to reach the PMT. The dark current contribution from the PMT was measured with a voltmeter for different high voltage settings.

The results, which are shown in table 7.1, confirm the assumptions that the contribution from the dark current is very small compared with the fluorescence from the paper samples or with the background caused by the lamp.

PMT high voltage/a.u.	Signal/V
0.0	0.0014
4.0	0.0014
5.0	0.0018
6.0	0.0032
7.0	0.0086
8.0	0.030

Table 7.1   Signal contribution from dark current of the PMT.

7.3.2 Room light contribution

As in the dark current measurements the light source was turned off. Due to the fact that the contribution of room light depends on the filter setup in front of the PMT, measurements were made with the two available interference filters. The room illumination used corresponds to that recommended during ordinary working conditions. The dependence on the optical properties of the measured sample was studied by using samples of either black cardboard or newsprint (with 25% DIP). The darkness signal is of course the same as the output voltage due to dark current.

From this investigation, with results shown in table 7.2, it can be concluded that the room light gives very little contribution to the signal (still having an accuracy of at least two valid decimal numbers) when having the high voltage control set between 0 and 3. If the narrow interference filter or an additional long pass filter is used the amplifier voltage can be increased further without losing the accuracy.

PMT high voltage/a.u.	0.0	1.0	2.0	3.0	4.0	5.0	6.0	7.0
Darkness signal/V	0.0014	0.0014	0.0014	0.0014	0.0014	0.0018	0.0032	0.0086
Room light signal/V Narrow interference filter, *black cardboard*	0.0014	0.0014	0.0015	0.0017	0.0028	0.0070	0.023	0.089
Broad interference filter, *black cardboard*	0.0014	0.0015	0.0020	0.0042	0.013	0.044	0.17	0.66
newsprint	0.0014	0.0015	0.0023	0.0054	0.018	0.067	0.25	0.99

Table 7.2   Signal contribution from room light.

7.3.3 Contribution from internal background light
and response on different support materials

The signals from different materials were measured at different amplifier voltages using any of the two interference filters. The lamp power was set to 80 W, and since the materials were intended as supports or background references the room light was turned off.

Barium sulphate, which is almost totally reflecting, has to be considered as the best background reference because of its having a scattering ability similar to that of paper. It has, however, a higher reflectance than paper. The measured values, listed in table 7.3.a, show some differences between the materials. Compared with the barium sulphate the black cardboard, the aluminium and the black painted aluminium give smaller values, while the cellulose (in form of filter papers) gives a very large signal. The large cellulose signal is of course due to fluorescence. As for the black cardboard, the black dye absorbs the light and prevents it from exciting fluorescent substances in the paper, hence giving a small signal. The aluminium surfaces on the other hand are good reflectors but have almost no scattering ability.

In order to investigate the change in background signal due to different filter setups including long pass filters, listed in the component list in section 6.2.1, additional measurements were made on barium sulphate under in other respects the same conditions. The results in table 7.3.b indicate that the long pass filter GG 400, which has its cut-off wavelength at 400 nm, has no impact when using the narrow interference filter (FWHM=10 nm), but some influence when using the broad filter (FWHM=40 nm). The data also implies that there is some background light in the blue region that should be minimised.

PMT high voltage/a.u.	0.0	1.0	2.0	3.0
Signal/V				
Narrow interference filter,				
barium sulphate	0.0051	0.021	0.095	0.41
cellulose	0.079	0.34	1.56	7.77
black cardboard	0.0017	0.0055	0.025	0.11
aluminium	0.0023	0.0075	0.034	0.15
black painted aluminium	0.0031	0.011	0.050	0.23
Broad interference filter,				
barium sulphate	0.018	0.076	0.37	1.63
cellulose	0.13	0.55	2.82	>10
black cardboard	0.0037	0.014	0.068	0.30
aluminium	0.0046	0.018	0.086	0.39
black painted aluminium	0.0074	0.031	0.15	0.68

Table 7.3.a Signals from different materials.

PMT high voltage/a.u.	0.0	1.0	2.0	3.0
Signal/V				
Narrow interference filter (NIF)	0.0051	0.021	0.095	0.41
NIF + GG 400	0.0055	0.021	0.096	0.40
NIF + GG 420	0.0037	0.014	0.062	0.26
Broad interference filter (BIF)	0.018	0.076	0.37	1.63
BIF + GG 400	0.015	0.062	0.30	1.35
BIF + GG 420	0.013	0.055	0.27	1.16

Table 7.3.b   Signals from a barium sulphate background when using different filter setups.

7.3.4 Filter setup for maximum signal-to-background ratio

The influence of the filter setups used in the previous test, according to table 7.3.b, on the S/B-ratio was investigated. A sample of barium sulphate was used as background reference. Measurements were made on newsprint samples made from TMP and DIP with DIP contents of 0% and 100%, respectively, in order to get a measure of the signal dependence on the FWA/lignin-ratio. The samples were moved at a speed of 5 mm/s, and measurements were made along a track of 100 mm in the machine direction of the paper, taking 4096 samples at a sampling frequency of 200 Hz. The lamp power was set to 80 W. The PMT high voltage control was at first set to values giving an 100% DIP signal in the interval 6-9.5 V for each filter setup (results shown in table 7.4.a), but in order to get a good overlook measurements were made at the same setting (i.e. a lower one for the narrow interference filter as well; results shown in table 7.4.b). Mean values and standard deviations were calculated for each sample and also the relative deviation in percent of the mean value. From the mean values and the background levels measured on bariumsulphate at the actual high voltage setting the S/B-ratio was calculated. The FWA/lignin-ratio was calculated as the ratio between the signal mean values from the samples containing 100% DIP and 0% DIP, respectively.

The results from the initial measurements, listed in tables 7.4.a and 7.4.b, clearly show that the S/B-ratio for the samples with 100% DIP is better for the narrow interference filter, which has a FWHM of 10 nm. Even though the S/B-ratio for the samples with 0% DIP is better in this case as well, the FWA/lignin-ratio seems to be larger for the narrow filter. This can be understood by considering the fact that the FWA has a narrower fluorescence spectrum compared with that of lignin, which also has its peak wavelength closer to the green region. The data also indicate that the long pass filter GG 420, with a cut-off wavelength at 420 nm, can increase the S/B-ratio and the FWA/lignin-ratio further. Additional measurements were made with the narrow interference filter setups, the results from which are shown in table 7.4.c. These show that the FWA/lignin-ratio is improved when using the GG 420 filter, and the best filter setup would then be the narrow interference filter combined with the long pass filter GG 420.

Filter setup	Sample	Signal/V mean, rel.dev.		Background signal/V	S/B-ratio	FWA/lignin-ratio
NIF + GG 400	0% DIP	1.02	7.7%	0.22	4.7	9.08
	100% DIP	9.30	4.9%		42	
NIF + GG 420	0% DIP	0.92	6.7%	0.15	6.2	10.0
	100% DIP	9.26	4.7%		62	

Table 7.4.a Signal ratios for different filter setups. *PMT high voltage setting = 2.60.*

Filter setup	Sample	Signal/V mean, rel.dev.		Background signal/V	S/B-ratio	FWA/lignin-ratio
NIF	0% DIP	0.198	9.1%	0.056	3.5	8.44
	100% DIP	1.67	2.9%		30	
NIF + GG 420	0% DIP	0.154	10.9%	0.045	3.4	10.8
	100% DIP	1.65	1.6%		37	
BIF	0% DIP	1.08	4.8%	0.86	1.3	6.44
	100% DIP	6.95	3.8%		8.1	
BIF + GG 400	0% DIP	0.950	5.2%	0.86	1.1	6.34
	100% DIP	6.02	3.1%		7.0	
BIF + GG 420	0% DIP	0.875	4.1%	0.70	1.3	6.68
	100% DIP	5.84	3.4%		8.3	

Table 7.4.b Signal ratios for different filter setups. *PMT high voltage setting = 1.70.*

Filter setup	Sample	Signal/V mean, rel.dev.		Background signal/V	S/B-ratio	FWA/lignin-ratio
NIF	0% DIP	1.02	3.0%	0.20	5.1	6.81
	100% DIP	6.97	4.6%		35	
NIF + GG 400	0% DIP	0.884	3.5%	0.16	5.5	7.77
	100% DIP	6.87	3.3%		43	
NIF + GG 420	0% DIP	0.784	4.1%	0.12	6.5	8.56
	100% DIP	6.71	1.9%		56	

Table 7.4.c Signal ratios for different filter setups. *PMT high voltage setting = 2.45.*

7.3.5 Output power at different lamp power settings
and influence of lamp power on signal and signal-to-background ratio

In order to investigate the influence of lamp power on the signal a sample of newsprint with 25% DIP, which is a quite ordinary percentage, was studied. The filter setup chosen on basis of the previous measurements was used, and measurements were made along the same distance on the paper and under the same sampling conditions as in the previous tests. The PMT high voltage control was set at 3.15, and the lamp power was varied from the maximum 100 W down to 40 W. Background signals from a barium sulphate sample were measured for the different lamp powers, and the S/B-ratio was calculated. It should be remembered that the background is somewhat overestimated, since barium sulphate has a higher reflectance than newsprint.

For the purpose in this project only a very small part of the total irradiated power from the lamp is used. Most of the power is lost in the water filter (the infrared region) and in the dichroic mirror of the beam turner (the visible region), but losses also appear in filters and lenses in the system. The actual output power from the equipment was measured with a power meter at the lamp power settings used. The measurements were made with the light focused on the detection area of the power meter.

The results are shown in table 7.5, and in figure 7.1 the signal values for paper samples and background are plotted versus the lamp power. From the output power values it can be concluded that about 0.1% of the lamp power exits as UV light through the bottom lens. Concerning the signal values there seems to be a linear relation between signal and lamp power for the measured sample, but the S/B-ratio can be regarded the same for all lamp power settings. From a signal-to-background point of view it is therefore unimportant which lamp power is chosen. Since as much fluorescence light as possible is wanted in order to get statistical advantages, the lamp power should be set as high as possible. On the other hand a higher power will induce additional decomposition of lignin and FWAs, resulting in a faster signal decrease when measuring on a certain spot. This latter fact can be ignored when having web speeds of real magnitudes, i.e. around 20 m/s. The lamp power is in these measurements not set to the maximum but to the sufficient power of 80 W, thereby also prolonging the life of the lamp.

Lamp power/W	Output power/W	Signal/V mean, st.dev.		Background signal/V	S/B-ratio
100	0.110	7.52	0.61	0.50	15
90	0.096	6.95	0.41	0.46	15
80	0.085	5.64	0.37	0.41	14
70	0.072	4.46	0.24	0.36	12
60	0.060	3.80	0.25	0.26	15
50	0.050	3.12	0.20	0.21	15
40	0.037	1.93	0.16	0.12	16

Table 7.5   Output power, signal values and S/B-ratios for different lamp power settings.
Measurements were made on 25% DIP samples and on barium sulphate (background).
*PMT high voltage setting = 3.15.*
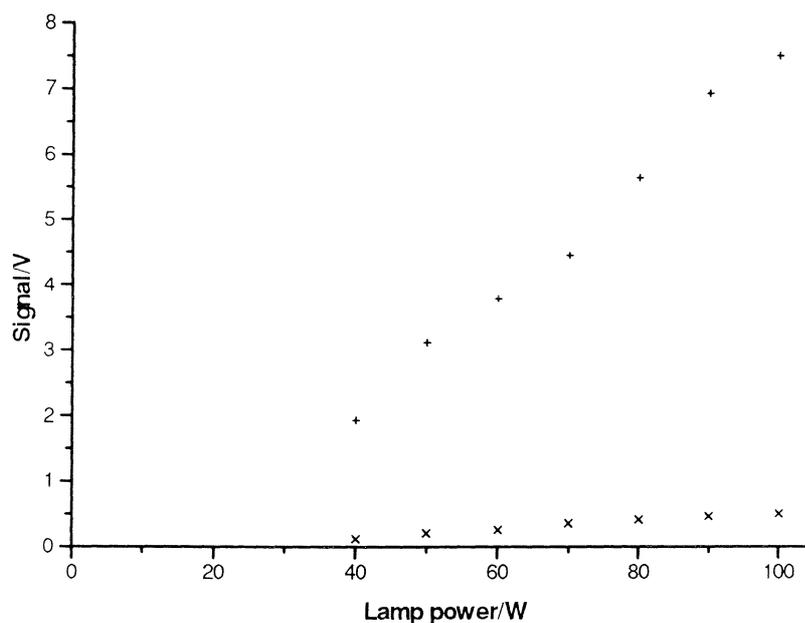
Fig. 7.1 Signal values from samples of newsprint with 25% DIP (+) and barium sulphate (x) at different lamp power settings. *PMT high voltage setting = 3.15*

7.3.6 Change in signal due to vertical paper displacement

In this investigation the signal was also registered for vertical sample displacements of 1 mm, 2 mm and 4 mm out of focus in both directions. Measurements were made on a piece of black cardboard and along a 100 mm track on a newsprint sample with 25% DIP.

The results are shown in table 7.6, and in figure 7.2 the signal values are plotted versus the distances from focus. Of course the signal change is larger for the newsprint sample, but the black cardboard sample gives the same signal behaviour overall. It can thus be concluded that the output voltage increases when the paper is displaced towards the bottom lens and decreased when displaced away from it. The explanation to this might be that the fluorescence light due to a larger spot size and more excited molecules can be transmitted all the way to the PMT tube in the former case, while in the latter it can not due to the light collection properties of the equipment. The signal change of about 0.3 V for the newsprint sample due to a displacement of 1 mm might be regarded as quite much, but it is still less than the standard deviation due to FWA distribution in the paper. Further the paper web displacements in real situations can be made much smaller than 1 mm, and the natural roughness of the paper surface also is much smaller. Any large impact on the signal from displacements out of focus should therefore not be expected from carefully performed measurements.

Tests were also made in which an iris diaphragm was used in order to increase the depth of field. This however did not lead to any improvement of the signal behaviour following displacement.

Distance from focus/mm	Signal/V *black cardboard*	Signal/V *newsprint, 25% DIP* mean, st. dev.	
-4	6.48	7.10	0.66
-2	6.30	6.50	0.72
-1	6.19	6.32	0.61
0	6.12	5.77	0.55
1	6.06	5.49	0.57
2	6.02	5.28	0.50
4	5.85	4.48	0.32

Table 7.6   Signal changes due to vertical paper displacements.
*PMT high voltage settings = 6.10 and 2.75, respectively.*
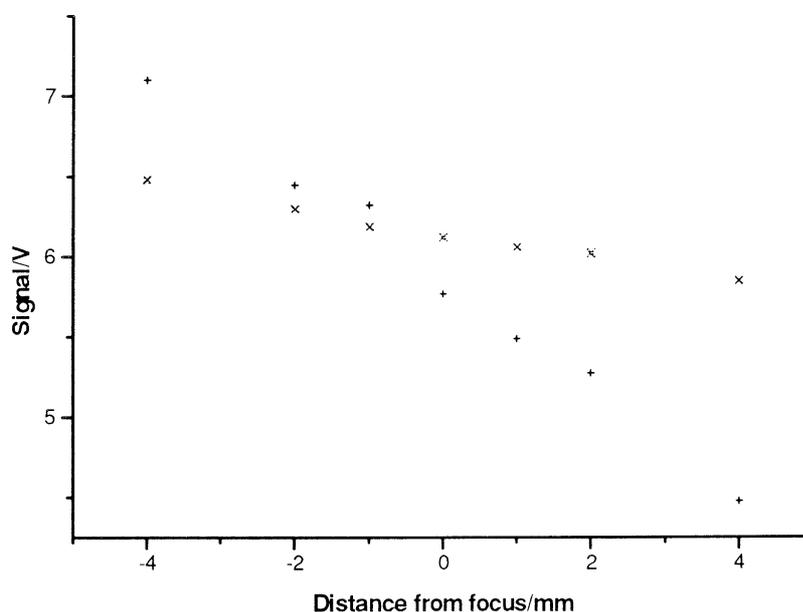
Fig. 7.2   Signal values from newsprint with 25% DIP (+) and black cardboard (x) at different distances from focus. *PMT high voltage settings = 2.75 (+) and 6.10 (x)*

7.3.7 Resolving power of the equipment

Optimisation of the beam quality resulted in a focused spot diameter of about 1.5 mm. In order to get a measure of how the fluorescence signal corresponds to this spot size a few different black and white patterns were designed and printed on copy paper. The patterns consisted of 0.2 mm wide white lines with black spacings of different widths according to figure 7.3. Measurements were made across these lines along a track of about 50 mm, taking 4096 samples at a sampling rate of 400 Hz. The PMT high voltage control was set to 1.05, resulting in approximate signal levels of 8 V from white areas and 0.6 V from black ones. As a measure of resolution the following criterion was applied: the white pattern is resolved when, with the zero level at 0.6 V, the signal from the black lines is at most half the value of the signal from the white lines.

Figures 7.4.a and 7.4.b show two measurements made over a pattern with 0.2 mm wide white lines separated by black lines of widths 0.2 mm, 0.4 mm, 0.6 mm, 0.8 mm, 1.3 mm and 1.8 mm, respectively. It can be seen that the signal from the white areas is affected by light from adjacent black areas, but the white lines can be discerned already at the spacing 0.6 mm. Using the resolution criterion, a spacing of between 1.3 mm and 1.8 mm is needed for resolution, and this corresponds very well to a spot size of 1.5 mm.
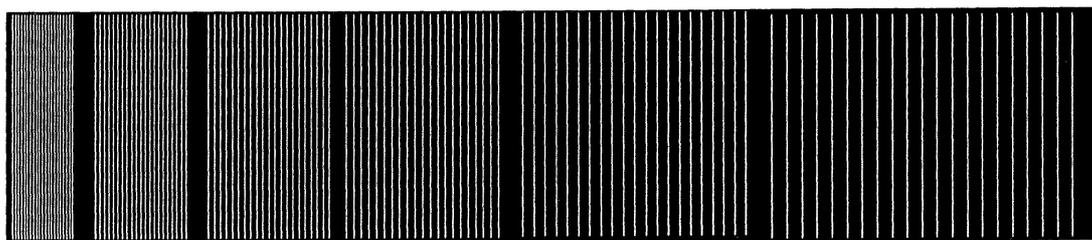
Fig. 7.3 Pattern, printed on copy paper, for resolution measurements consisting of 0.2 mm wide white lines with black spacings of widths 0.2 mm, 0.4 mm, 0.6 mm, 0.8 mm, 1.3 mm and 1.8 mm, respectively.
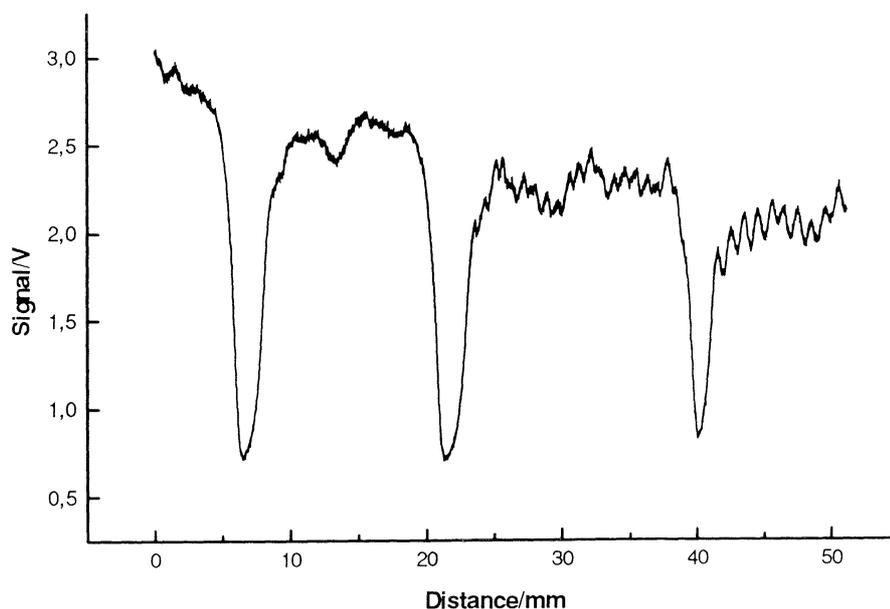
Fig. 7.4.a Resolution measurements on the first four groups of lines in the pattern showed in figure 7.3. *PMT high voltage setting = 1.05.*
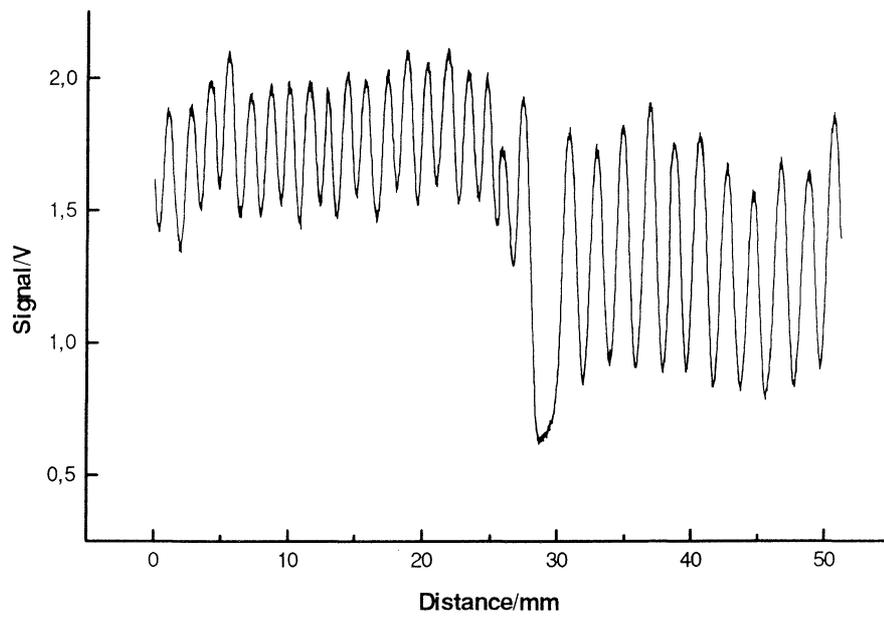
Fig. 7.4.b Resolution measurements on the last two groups of lines in the pattern shown in figure 7.3. *PMT high voltage setting = 1.05.*

8 Testing of the signal response
on paper samples of varying composition

8.1 Measurements on samples
with respect to the signal response on different substances

These measurements were made in order to investigate the magnitude of the fluorescence signal for different percentages of DIP in newsprint, but also the response on other substances. The dependence on lignin content was studied by using laboratory sheets made from pulps with different lignin percentages, and the signal response on sheets made from pulp bleached in different ways was also tested. In order to get an opinion of the influence of fillers, paper samples made of bleached pulp with different percentages of fillers added were measured on.

Multiple measurements, along different tracks, were made for each sample in order to get statistically more reliable values. The means and standard deviations of the recorded signals were used to calculate mean signal properties for each sample:

$$m = \frac{1}{k}(m_1 + m_2 + ... + m_k) \tag{8.1}$$

$$\sigma = \sqrt{\frac{n-1}{kn-1}(s_1^2 + s_2^2 + ... + s_k^2)} \approx \sqrt{\frac{1}{k}(s_1^2 + s_2^2 + ... + s_k^2)} \tag{8.2}$$

where m denotes the mean of the signal, s the variance, σ the standard deviation, n the number of samples per recording (here: 4096) and k the number of recordings. The latter part of equation (8.2) is valid, as in this case, when n is large.

8.1.1 Signal response on samples with different lignin percentages

The samples used in this test were hand made laboratory sheets made from mixtures of kraft pulp (KP, bleached sulphate pulp) and TMP. Since the kraft pulp has a lignin content of about 0.3-1% and the TMP contains about 30% lignin, a variation in lignin content between the samples could be achieved by varying the relative content of the two pulp types. Measurements were made on two equal series of samples, each covering the range 0-100% TMP. Over a distance of about 50 mm, 4096 data samples were taken with a sampling frequency of 400 Hz. For each recording means and standard deviations were calculated, and the mean signal properties were obtained through equations (8.1) and (8.2).

The results are shown in table 8.1, and the signal values are also plotted versus the TMP content in figure 8.1. Since the kraft pulp only contains about 1% lignin, the TMP percentage scale can be regarded as linear also with respect to lignin percentage. It might at first seem surprising that the signal decreases with increasing lignin content, but this has an explanation: the samples measured on, maybe even the ones without TMP, contains enough lignin for self-absorption to occur (see section 3.2.2). This behaviour has been observed before during fluorescence measurements on black liquor samples with different lignin concentrations [21]. As mentioned in section 5.2, the obvious fact that the self-absorption following excitation with UV light is so dominant at the

lignin percentages occuring in newsprint, speaks for the advantage of performing lignin distribution measurements through excitation with red light [15].

An interesting question related to the observation made is if any of the fluorescence light from FWAs in paper containing recycled fibre is absorbed by lignin molecules, and if so to what extent. This will be touched upon in section 8.2.

TMP content/%	Signal/V					
	Series 1 mean, st.dev.		Series 2 mean, st.dev.		*Mean signal* mean, st.dev.	
0	7.27	0.34	7.60	0.17	7.44	0.19
10	4.05	0.19	4.51	0.23	4.28	0.25
20	2.90	0.21	3.16	0.16	3.03	0.17
30	2.66	0.09	2.89	0.28	2.77	0.28
40	2.34	0.10	2.43	0.10	2.39	0.10
50	1.82	0.10	2.05	0.10	1.94	0.10
60	1.64	0.05	1.91	0.17	1.78	0.12
70	1.67	0.06	1.86	0.24	1.77	0.24
80	1.47	0.06	1.47	0.05	1.47	0.05
90	1.38	0.05	1.33	0.05	1.36	0.05
100	1.16	0.04	1.13	0.06	1.15	0.06

Table 8.1 Signal response on laboratory sheets containing different percentages of lignin. *PMT high voltage setting = 2.60.*
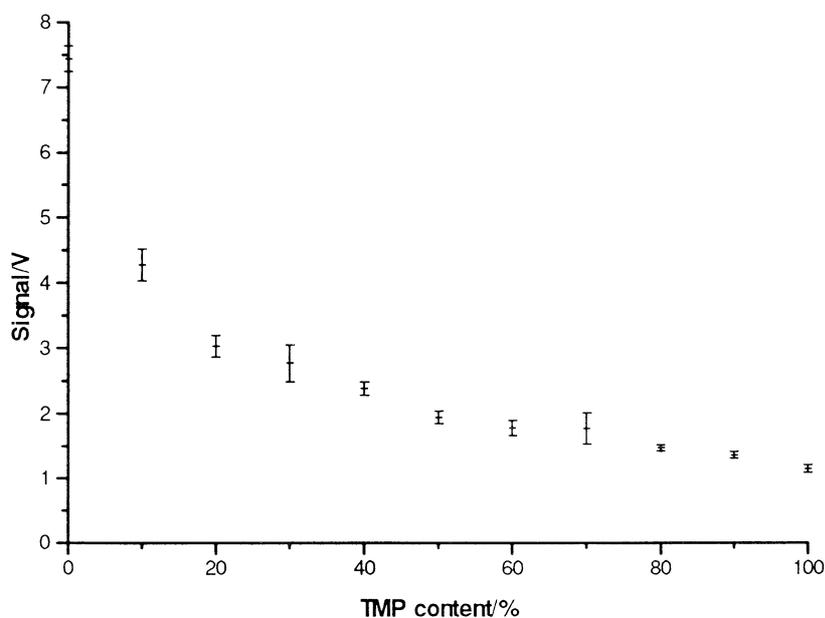
Fig. 8.1 Signal response on laboratory sheets containing different percentages of lignin. *PMT high voltage setting = 2.60.*

8.1.2 Signal response on samples made from chemical pulp bleached to a certain extent

Depending on the bleaching process used, the lignin is removed or decomposed to a varying extent, hence resulting in varying lignin content in the pulp. Laboratory sheets made from sulphate and sulphite pulps of three different bleaching grades were measured on under the same recording conditions as in the previous test. The samples made from oxygen bleached pulp have the largest lignin content, the ones made from pre-bleched pulp a smaller content and the samples made from bleached pulp the smallest content of lignin.

The measured values and the mean signal values, obtained through equations (8.1) and (8.2), are listed in table 8.2. The kappa number, which is a measure of the lignin content in the pulp, for each sample is also listed. As in the previous test the signal magnitude is larger for samples containing less lignin, beacause of self-absorption.

Pulp type	Kappa number	Signal/V					
		Series 1 mean, st.dev.		Series 2 mean, st.dev.		Mean signal mean, st.dev.	
Oxygen bleached sulphate pulp	19.50	1.54	0.17	1.32	0.04	1.43	0.13
Pre-bleached sulphate pulp	6.40	4.44	0.16	4.60	0.09	4.52	0.13
Bleached sulphite pulp	3.00	8.59	0.24	8.42	0.29	8.51	0.26

Table 8.2   Signals from laboratory sheets made from pulps with different degrees of bleaching. *PMT high voltage setting = 2.60*

8.1.3 Signal response on newsprint samples containing different amounts of recycled fibre

This investigation was made using sample series from three Swedish newsprint mills, denoted A, B and C. The samples were made from DIP and a mixture principally consisting of TMP, and they were delivered in sheets of A4 size. To the samples from mill C clay had been added, corresponding to a content of 1%. Each sample was measured on in the machine direction along three tracks, separated by a few centimetres, in order to include the statistical variation in the cross direction as well. Measurements were made over a distance of about 100 mm, taking 4096 samples at 200 Hz.

The measured values are listed in tables 8.3.a-c. In figures 8.2.a-c the values for the calculated mean signals are plotted versus the DIP content, and least-squares linear fits have also been made. All series show good linear behaviour, and the equations of the fitted lines are in fact almost the same except for a different offset value for the series from mill C. So far it can thus be concluded that the signal response for recycled fibre is very good when, as in this case, measurements are made on samples with an in other respects unvaried composition. It must however be kept in mind that the composition of the DIP used in production may vary depending on the source of the recycled paper. To what extent a good response is maintained when measuring on newsprint samples with a more varying composition, will be investigated in following measurements, discussed in section 8.2.

DIP content/%	Signal/V							
	Track 1 mean, st.dev.		Track 2 mean, st.dev.		Track 3 mean, st.dev.		*Mean signal* mean, st.dev.	
0	1.42	0.11	1.51	0.07	1.51	0.07	1.48	0.09
5	1.56	0.14	1.68	0.12	1.74	0.12	1.66	0.13
10	2.02	0.19	2.08	0.17	2.16	0.19	2.09	0.18
25	4.29	0.33	4.41	0.39	4.67	0.53	4.46	0.43
30	5.05	0.48	4.90	0.47	5.36	0.53	5.11	0.49
35	5.43	0.59	5.67	0.49	5.48	0.50	5.53	0.53
60	7.29	0.53	7.38	0.54	7.69	0.49	7.45	0.52

Table 8.3.a Signal response on newsprint with varying DIP content, produced at mill A. *PMT high voltage setting = 2.60.*

DIP content/%	Signal/V							
	Track 1 mean, st.dev.		Track 2 mean, st.dev.		Track 3 mean, st.dev.		*Mean signal* mean, st.dev.	
0	1.45	0.15	1.70	0.08	1.65	0.09	1.60	0.11
10	2.37	0.20	2.45	0.28	2.46	0.22	2.42	0.24
20	3.54	0.32	3.59	0.30	3.61	0.37	3.58	0.33
30	4.66	0.35	4.86	0.34	4.83	0.38	4.78	0.36
40	6.40	0.80	6.36	0.71	6.22	0.51	6.33	0.69
50	6.73	0.53	7.18	0.54	6.96	0.49	6.96	0.52

Table 8.3.b Signal response on newsprint with varying DIP content, produced at mill B. *PMT high voltage setting = 2.60.*

DIP content/%	Signal/V							
	Track 1 mean, st.dev.		Track 2 mean, st.dev.		Track 3 mean, st.dev.		*Mean signal* mean, st.dev.	
15	3.20	0.43	3.68	0.58	3.25	0.38	3.37	0.47
30	5.51	0.70	5.56	0.60	5.27	0.72	5.45	0.68
45	6.49	0.58	6.98	0.71	6.94	0.74	6.80	0.68
60	8.23	0.63	8.74	0.56	8.37	0.55	8.45	0.58

Table 8.3.c Signal response on newsprint with varying DIP content, produced at mill C. *PMT high voltage setting = 2.60.*
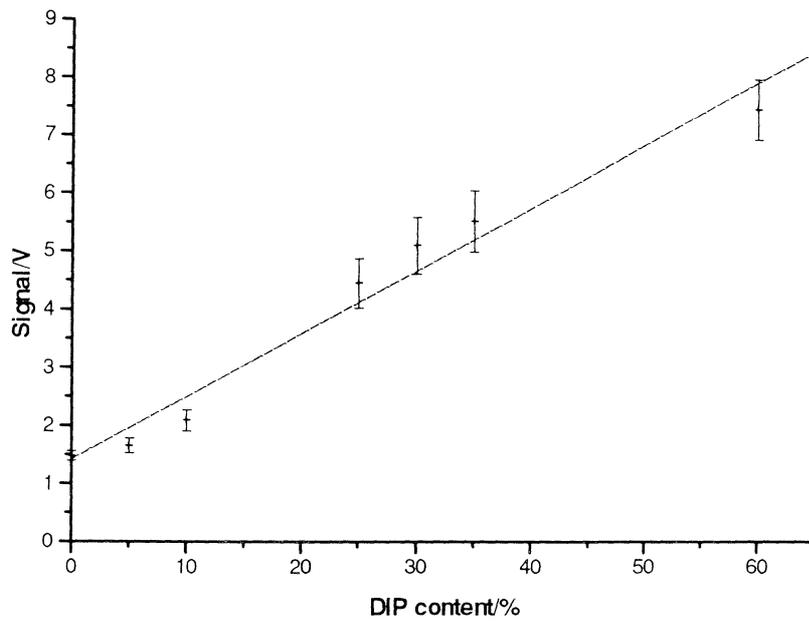
Fig 8.2.a Signal response on newsprint with varying DIP content, produced at mill A.
The measured values are listed in table 8.3.a. The equation of the fitted line is
(Signal/V) = 1.42 + 0.108·(DIP content/%). *PMT high voltage setting = 2.60.*
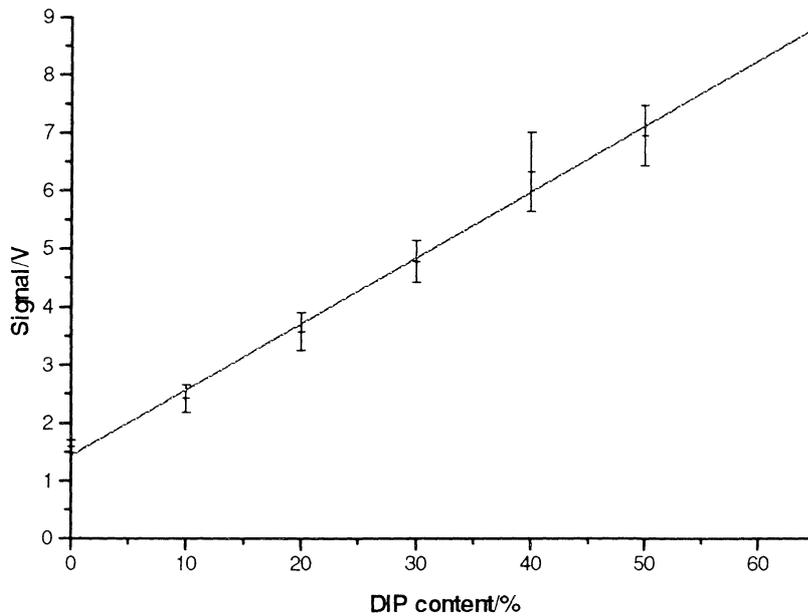
Fig. 8.2.b Signal response on newsprint with varying DIP content, produced at mill B.
The measured values are listed in table 8.3.b. The equation of the fitted line is
(Signal/V) = 1.44 + 0.113·(DIP content/%). *PMT high voltage setting = 2.60.*

39
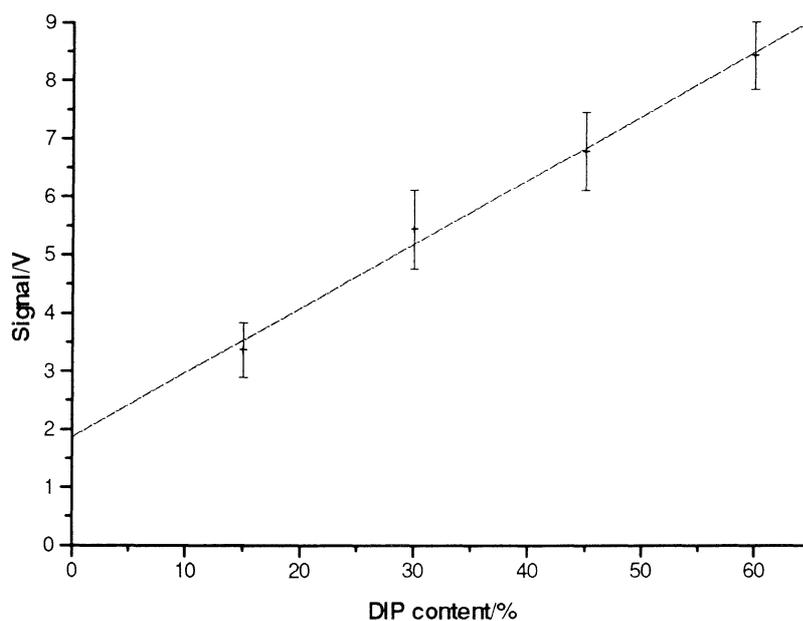
Fig. 8.2.c   Signal response on newsprint with varying DIP content, produced at mill C.
The measured values are listed in table 8.3.c. The equation of the fitted line is
(Signal/V) = 1.88 + 0.110·(DIP content/%). *PMT high voltage setting = 2.60.*

8.1.4 Signal response on paper containing different amounts of fillers

The samples studied were made from bleached pine sulphate pulp with fillers added in different amounts. Two series were measured on, containing calcium carbonate (from marble) and PCC (precipitated calcium carbonate; see section 3.3.4), respectively. Each sample was measured on along two tracks, taking 4096 samples at 200 Hz over a distance of about 100 mm.

From the results, listed in tables 8.4.a and 8.4.b, it appears that there is a general decrease in signal following increasing filler content. The only exception is in the case of 10% $CaCO_3$, where a signal increase is noticed. Trying to explain the behaviour, it must firstly be considered that the only likely source of fluorescence is cellulose, and to some extent impurities in the marble $CaCO_3$. The PCC is synthetically produced and should therefore exhibit no fluorescence. Thus the signal decrease for the samples containing PCC might be due to the decreased concentration of cellulose in the paper following a larger filler content. This is probably also the case for the samples containing marble $CaCO_3$, but the presence of fluorescent impurities may result in a smaller signal decrease.

The fluorescence is however only part of the explanation, since scattering and absorption properties are important when fillers are involved. It is hazardous to make any conclusions about the effect of fillers on the signal from newsprint, since the composition is more complex in that case.

CaCO₃ content/%	Signal/V					
	Sample 1 mean, st.dev.		Sample2 mean, st.dev.		Mean signal mean, st.dev.	
0	7.36	0.54	7.37	0.38	7.36	0.47
10	7.85	0.29	8.29	0.42	8.07	0.36
20	6.03	0.30	6.65	0.23	6.34	0.26
30	6.09	0.37	6.12	0.48	6.11	0.43

Table 8.4.a Signal response on different $CaCO_3$ content in paper made from bleached sulphate pulp. *PMT high voltage setting = 3.00.*

PCC content/%	Signal/V					
	Sample 1 mean, st.dev.		Sample 2 mean, st.dev.		Mean signal mean, st.dev.	
0	7.36	0.54	7.37	0.38	7.36	0.47
10	6.72	0.33	7.18	0.53	6.95	0.44
20	5.64	0.26	5.72	0.20	5.68	0.23
30	5.04	0.26	4.72	0.18	4.88	0.23

Table 8.4.b Signal response on different PCC content in paper made from bleached sulphate pulp. *PMT high voltage setting = 3.00.*
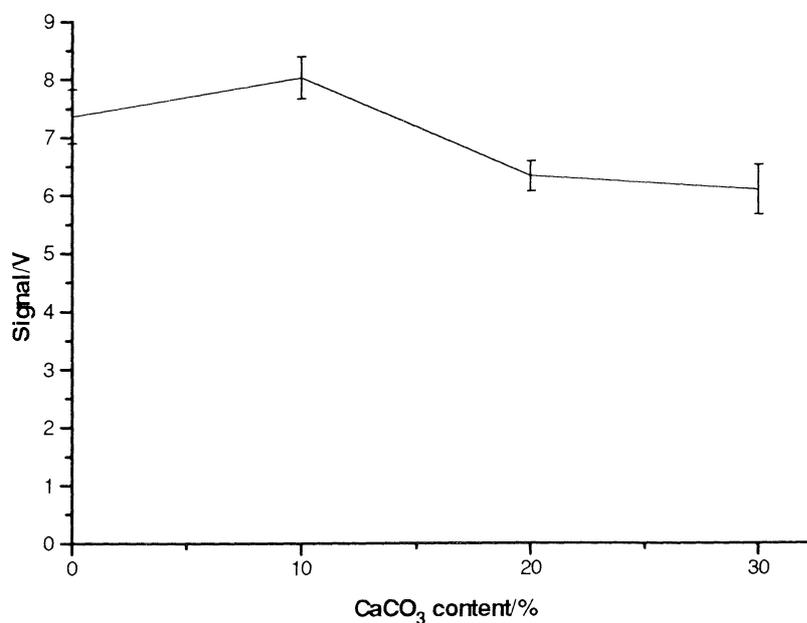
Fig. 8.3.a Signal response on different $CaCO_3$ content in paper made from bleached sulphate pulp. *PMT high voltage setting = 3.00.*

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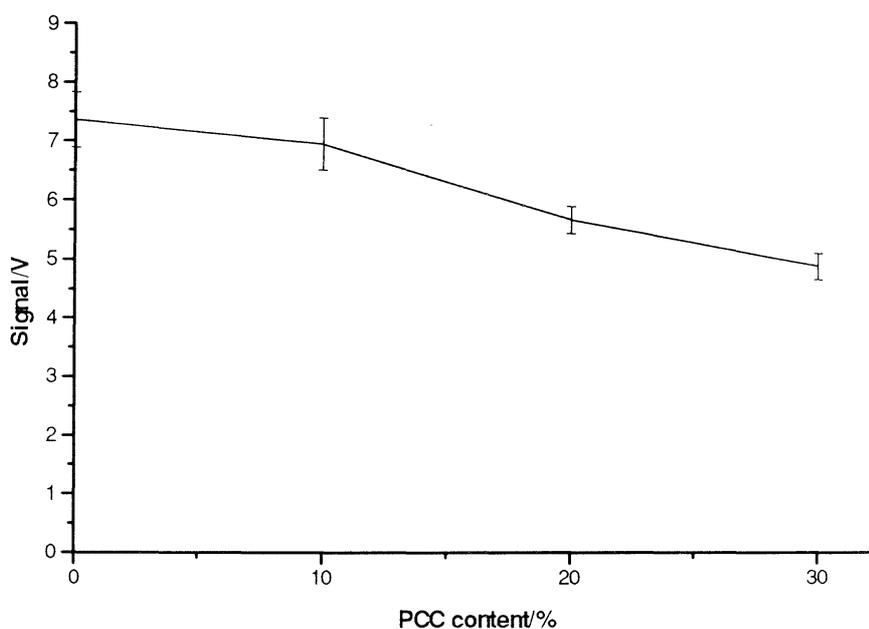
Fig. 8.3.b   Signal response on different PCC content in paper made from bleached sulphate pulp.
PMT high voltage setting = 3.00.

8.2   Measurements on newsprint samples from production

These studies were performed in order to investigate the signal response on newsprint with a more complex composition than that of the samples discussed in section 8.1.3. The samples, which were newsprint produced at mill B, were made from a varying pulp mixture consisting of DIP, chemical pulp, waste pulp and to the major part mechanical pulp. The waste pulp consists of waste material from the production that is brought back into the stock. Measurements were made in the same way and under the same conditions as the tests discussed in section 8.1.3.

The results from the measurements are shown in table 8.5, and in figure 8.4 the signal values are plotted versus the DIP content. Figure 8.4 clearly shows that, depending on the composition, there may be differences between the signal values from samples having nearly the same DIP content. For instance, samples no. 5 and 6 have the same composition and show good signal correspondance, while samples no. 3 and 4, having small differences in composition, exhibit significant differences in signal value. The signal value from sample 8 is interesting since, in the studies discussed in section 8.1.3, a DIP content of 60% was needed to produce a signal value of the same magnitude. A possible explanation is that since the content of mechanical pulp in sample 8 is comparatively low, the effect from self-absorption of lignin is reduced. The explanation of the differences in each case is however not easy to find just on basis of composition data.

Sample	DIP content/%	Signal/V							
		Track 1 mean, st. dev.		Track 2 mean, st. dev.		Track 3 mean, st. dev.		*Mean signal* mean, st. dev.	
1	31	5.74	0.75	5.88	0.55	5.86	0.63	5.83	0.65
2	28	5.04	0.40	4.85	0.44	4.95	0.47	4.95	0.44
3	24	5.75	0.44	5.54	0.53	5.85	0.48	5.72	0.48
4	24	7.30	0.35	7.38	0.36	7.39	0.35	7.36	0.35
5	21	6.11	0.55	6.35	0.69	6.32	0.52	6.26	0.59
6	21	6.27	0.59	6.48	0.57	6.32	0.50	6.35	0.56
7	23	7.49	0.52	7.13	0.64	7.12	0.62	7.25	0.60
8	37	9.29	0.29	9.41	0.21	9.31	0.24	9.34	0.25

Table 8.5 Signal values measured on the samples discussed in section 8.2.
PMT high voltage setting = 2.60.
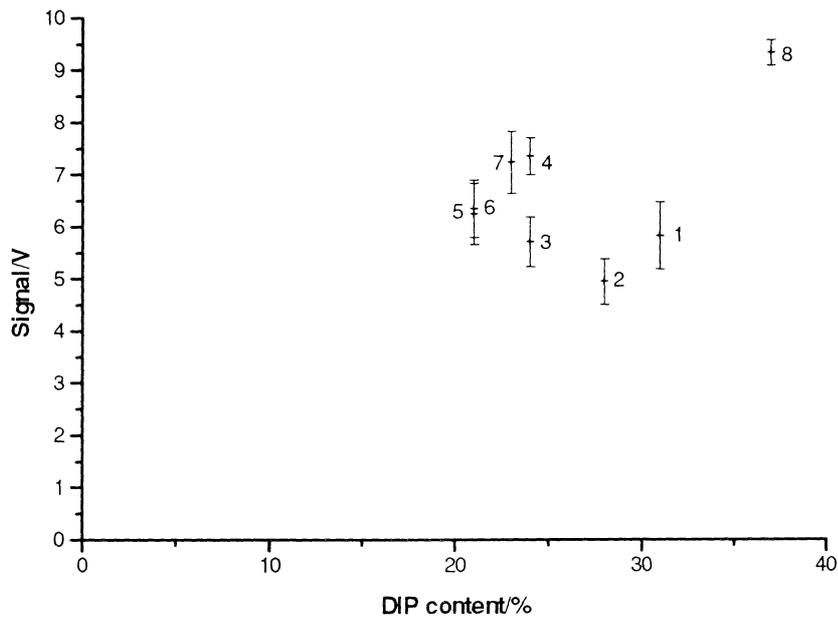
Fig. 8.4 The signal values from the samples listed in table 8.5 plotted versus the DIP content.
PMT high voltage setting = 2.60.

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8.3 Reproducibility of the fluorescence signal and investigation of differences in the fluorescence from the top and back sides of the paper

The first part of this investigation, made in order to confirm that the variations in the output signal is due not to random phenomena but to a variation in the local fluorescence properties, was made on four different samples containing DIP and two samples containing no DIP. The samples, which were taken from sample series measured on in other parts of the project, are listed in table 8.6. Measurements were made in the machine direction along two tracks, taking 4096 samples at 200 Hz over a distance of about 100 mm, and for each track two recordings were made. The tracks were marked at both ends and a piece of black tape was put at the beginning of each track in order to make it possible to match the two recordings. Mean values and standard deviations were calculated for each recording, and the output signals were plotted pairwise.

The second part of the study was completed by repeating the measurements for the reverse side of the sheets. Since the tracks were carefully marked at both ends, measurements could be made along the same track as on the other side. Only for the last two samples in table 8.6 it was known which side was the top side.

In table 8.7 the results of the measurements are shown, and some of the recordings are plotted in figures 8.5-8.7. In the first place it can be noticed that the signal is highly reproducible, since the signal pattern from the first recording appears to be the same in the second one. Thus it can be concluded that the recorded signal depends on systematic variations in the paper. This means that the measured standard deviation shows the variations in the paper and not the uncertainty of the measurements. The only obvious difference between two recordings is that the signal magnitude is somewhat lower in the second recording, especially in the case of 0% DIP. This is probably due to decomposition of essentially lignin in the paper, because of the intense UV light following the low paper speed. Differences may also occur by measuring slightly off the track the second time.

As for differences between the top and back sides of the paper, some of the samples show quite large differences in signal level. Samples 5 and 6 however give contradictory results on which side exhibits a larger signal magnitude. This may indicate that the distribution differences varies between different parts of the paper surface. Retention differences between the recycled fibre and the other fibres, because of the larger amount of fines in the recycled fibre, could explain a higher fluorescence intensity from the back side. The variation within each paper sample must however be considered. It has to be emphasised that more extensive measurements are needed in order to investigate differences over larger surfaces.

In addition to these observations it should be noticed that, when comparing the plotted recordings made on the top and back sides, there does not seem to be any obvious local correspondance between the distributions.

Sample	Description	Reference
1	Mill B 24% DIP, from production	Sample no. 4 in table 8.5
2	Mill B 50% DIP, test sample	Table 8.3.b
3	Mill B 0% DIP, test sample	Table 8.3.b
4	Mill A 0% DIP, test sample	Table 8.3.a
5	Mill A 23% DIP, from production	Sample no. 2 in table 9.1
6	Mill A 26% DIP, from production	Sample no. 6 in table 9.1

Table 8.6 Specification of the samples used in the measurements discussed in section 8.3.

Sample	Side	Track 1 Recording 1 mean, st. dev.		Track 1 Recording 2 mean, st. dev.		Track 2 Recording 1 mean, st. dev.		Track 2 Recording 2 mean, st. dev.	
1	1	7.39	0.33	7.53	0.41	8.07	0.76	7.85	0.76
	2	6.48	0.46	6.34	0.47	7.44	0.52	7.22	0.52
2	1	7.32	0.21	7.24	0.23	7.35	0.22	7.30	0.25
	2	8.06	0.26	7.97	0.28	7.93	0.28	7.75	0.31
3	1	5.35	0.25	4.89	0.20	5.40	0.29	4.85	0.27
	2	5.02	0.51	4.71	0.35	5.56	0.35	4.96	0.31
4	1	4.47	0.16	3.98	0.14	4.21	0.12	3.79	0.10
	2	4.10	0.15	3.71	0.14	3.96	0.11	3.56	0.10
5	top	5.32	0.52	5.25	0.56	5.65	0.44	5.38	0.46
	back	6.04	0.43	5.65	0.44	5.73	0.57	5.52	0.53
6	top	6.38	0.43	6.15	0.49	6.13	0.49	6.07	0.47
	back	5.86	0.46	6.14	0.49	5.61	0.47	5.33	0.47

Header for table: **Signal/V**

Table 8.7 Signal values obtained from measurements on the samples listed in table 8.7. *PMT high voltage settings = 2.60 (samples 1 and 2), 3.20 (samples 3 and 4) and 2.50 (samples 5 and 6).*
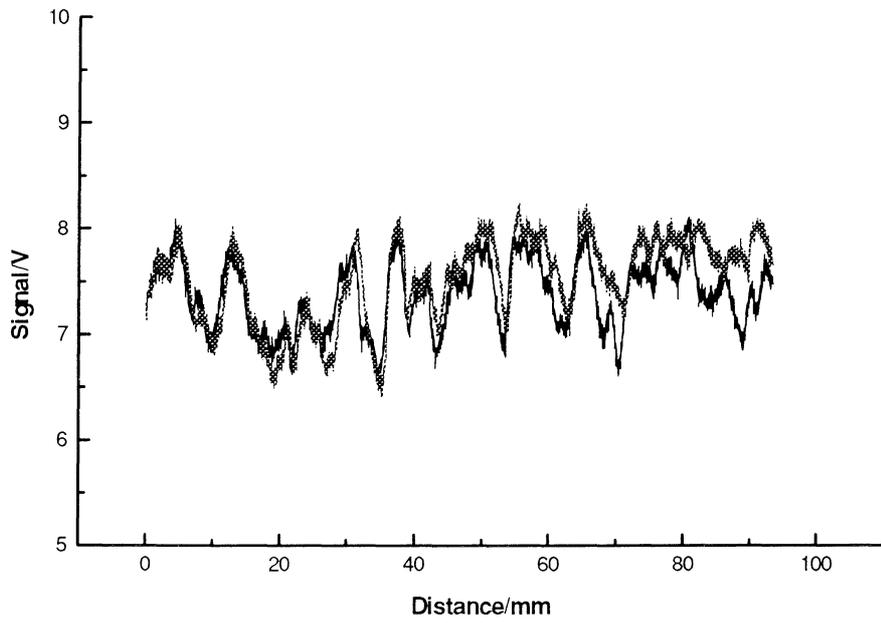
Fig. 8.5.a   Signal recording made on side 1 of sample 1 (track 1) in tables 8.7 and 8.8.
PMT high voltage setting = 2.60.
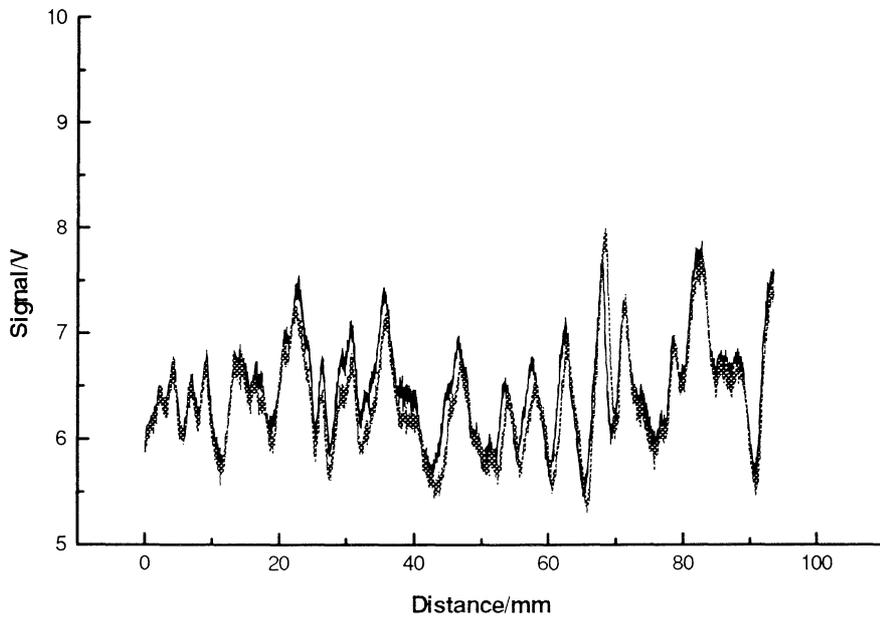
Fig. 8.5.b   Signal recording made on side 2 of sample 1 (track 1) in tables 8.7 and 8.8.
PMT high voltage setting = 2.60.

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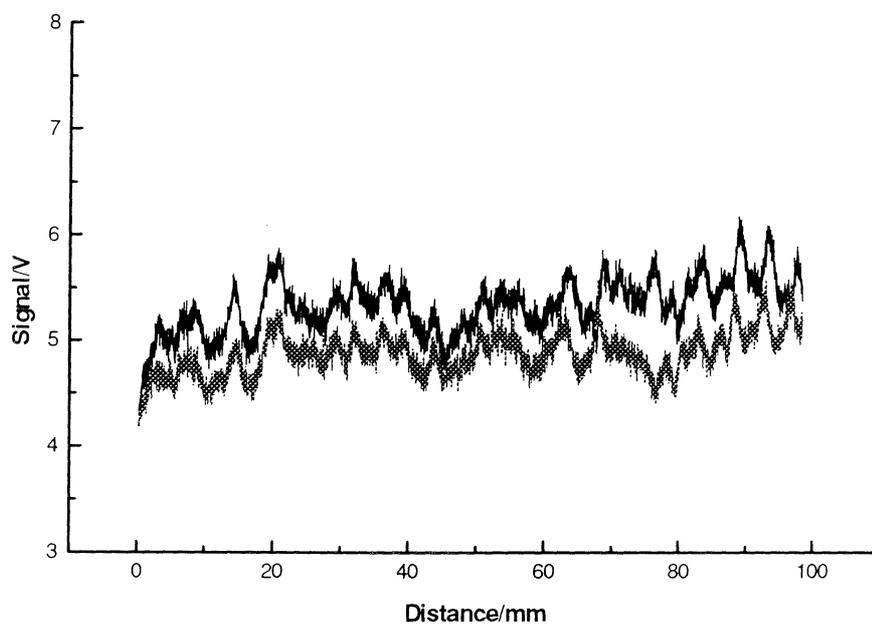
Fig. 8.6.a   Signal recording made on side 1 of sample 3 (track 1) in tables 8.7 and 8.8.
PMT high voltage setting = 3.20.
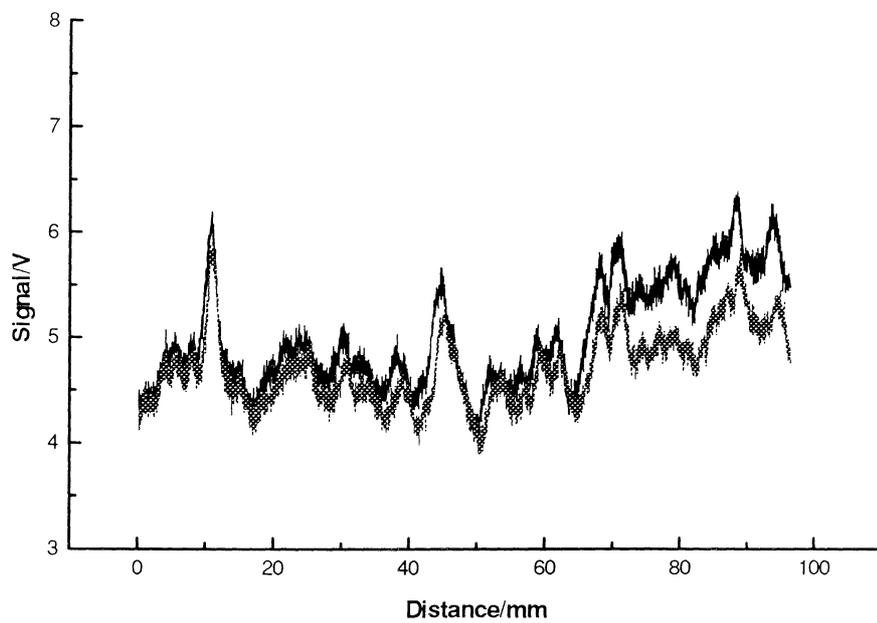
Fig. 8.6.b   Signal recording made on side 2 of sample 3 (track 1) in tables 8.7 and 8.8.
PMT high voltage setting = 3.20.

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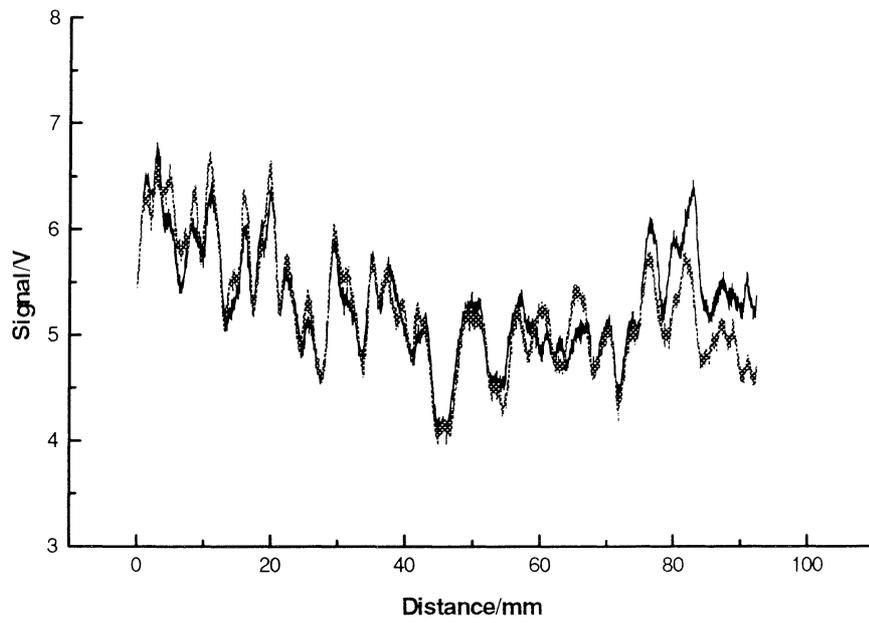
Fig. 8.7.a Signal recording made on the top side of sample 5 (track 1) in tables 8.7 and 8.8. *PMT high voltage setting = 2.50.*
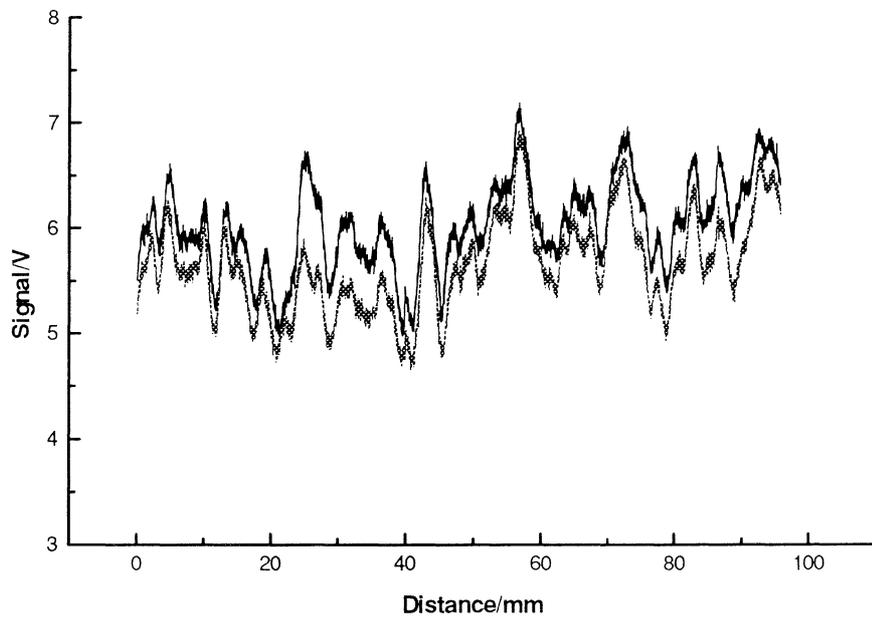
Fig. 8.7.b Signal recording made on the back side of sample 5 (track 1) in tables 8.7 and 8.8. *PMT high voltage setting = 2.50.*

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9 Measurements on long paper strips from a newsprint mill

The measurements discussed in this chapter were made in order to test the equipment in an application similar to the real on-line situation. The intention was also to investigate if any differences in paper composition and distribution of recycled fibre between the samples could be detected. The occurence of differences between the cross/machine directions and top/back sides of the paper was also investigated.

9.1 Measurement arrangements

For the purpose of running long paper strips under the equipment, a paper feeder was constructed according to figure 9.1. The desire was to run the strips at a speed in the range 0.1-0.3 m/s and also to have the possibility of simultaneously measuring the distribution of recycled fibre and lignin (with the lignin meter, see section 5.2). The paper feeder is built up around a carriage on which two tabletops, separated by a gap of some 30 cm, have been placed. The measurements are made in the gap over an aluminium plate (2), which is black painted because of the large penetration depth of the red light used in the lignin measurements. The aluminium plate is mounted on a vertically adjustable table. At the one end of the carriage a rubber-covered roll (1) is placed, driving the paper over the measurement plate from a pair of adjustable guiding cylinders, made of aluminium, at the other end (3). The roll is driven by a DC motor, supplied with a gear mechanism to give 100 rpm at 12 V. This results in a web speed of 0.19 m/s, measured by sampling with the AD-converter over a certain distance on a strip.
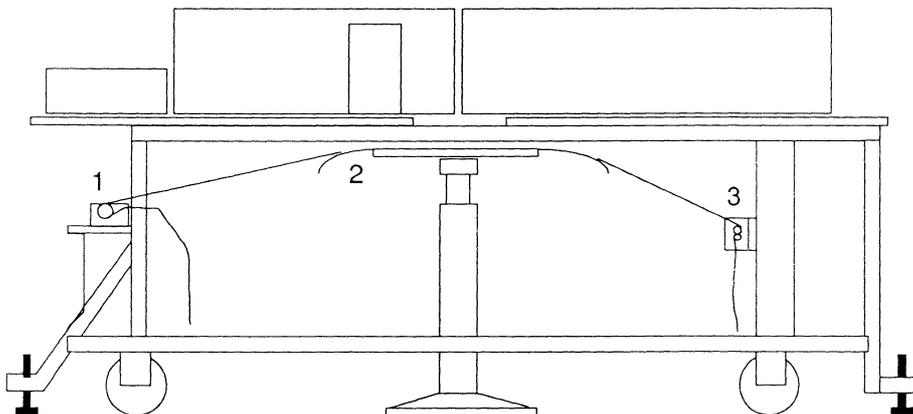
Fig. 9.1   Drawing of the paper feeder used for measurements on strips from paper machines, also showing the two fluorescence meters for recycled fibre and lignin.
(1) Roll driven by a DC motor, (2) Black painted aluminium plate mounted on a vertically adjustable table, (3) Guiding cylinders.

9.2 Measurements and results

The samples measured on were taken from a paper machine at mill A (see section 8.1.3). They originated from newsprint of somewhat varying composition, produced during different days. Samples from the same day were taken in the machine and cross directions (MD and CD) of the paper web, and they were 8 m long and 30-40 cm wide. The CD strips were of full length, thereby making it possible to detect any differences between the centre and the edges of the web. The DIP content was the same for samples taken the same day, but since they were taken at different hours their remaining composition varied. Samples 3 and 4 however had exactly the same composition.

In order to make it possible to measure over the full length of the strips, they were lengthened at both ends and furnished with markings at the joints. Measurements were made at a sampling rate of 1000 Hz, resulting in some 43000 samples from each strip. A low pass filter with a cut-off frequency of about 400 Hz was used in order to suppress aliasing. Each strip was measured on both top and back sides, and all measurements were made starting at the foreside of the strips.

In figures 9.3-9.8, on pages 52-57, the signal recordings are shown, and in table 9.1 the calculated means and standard variations are listed. The data again give reasons to believe that there is an unequal distribution between the sides of the paper, as was noticed in section 8.3.

From the plotted signal recordings variations of different periodicity can be observed. There seems to be large-scale variations with periods somewhere in the range 0.5-1 m, but also local high-intensity variations occuring more frequently. Trying to find some of these frequencies in the signals, the power spectral densities were calculated, but no further information was gained. Typical spectra, from samples 3 and 4, are shown in figure 9.2. The spectra from the other samples were not significantly differing from these ones. Since the spectra were very rich in low frequencies, it was impossible to detect the large-scale variations. Frequency analysis is otherwise an important tool in the search for distribution phenomena originating from production conditions.

Another interesting observation is that the signal variation, both from the top and back sides, seems to be smaller for samples containing more DIP. Comparing samples 3 and 4, an obviously larger variation in the machine direction than in the cross direction can also be noticed. In order to make general statements about this, repeated measurements should be performed on more MD and CD samples of equal composition.

Sample	Direction	DIP content/%	Signal/V			
			Top side mean, st. dev.		*Back side* mean, st. dev.	
1	CD	23	6.34	0.30	6.46	0.35
2	MD	23	5.55	0.24	5.79	0.25
3	CD	32	6.80	0.16	6.95	0.16
4	MD	32	6.85	0.22	7.06	0.22
5	CD	26	6.00	0.51	6.04	0.20
6	MD	26	6.33	0.26	6.00	0.24

Table 9.1   Signal values obtained from the measurements on newsprint strips discussed in section 9.2. *PMT high voltage setting = 2.50.*
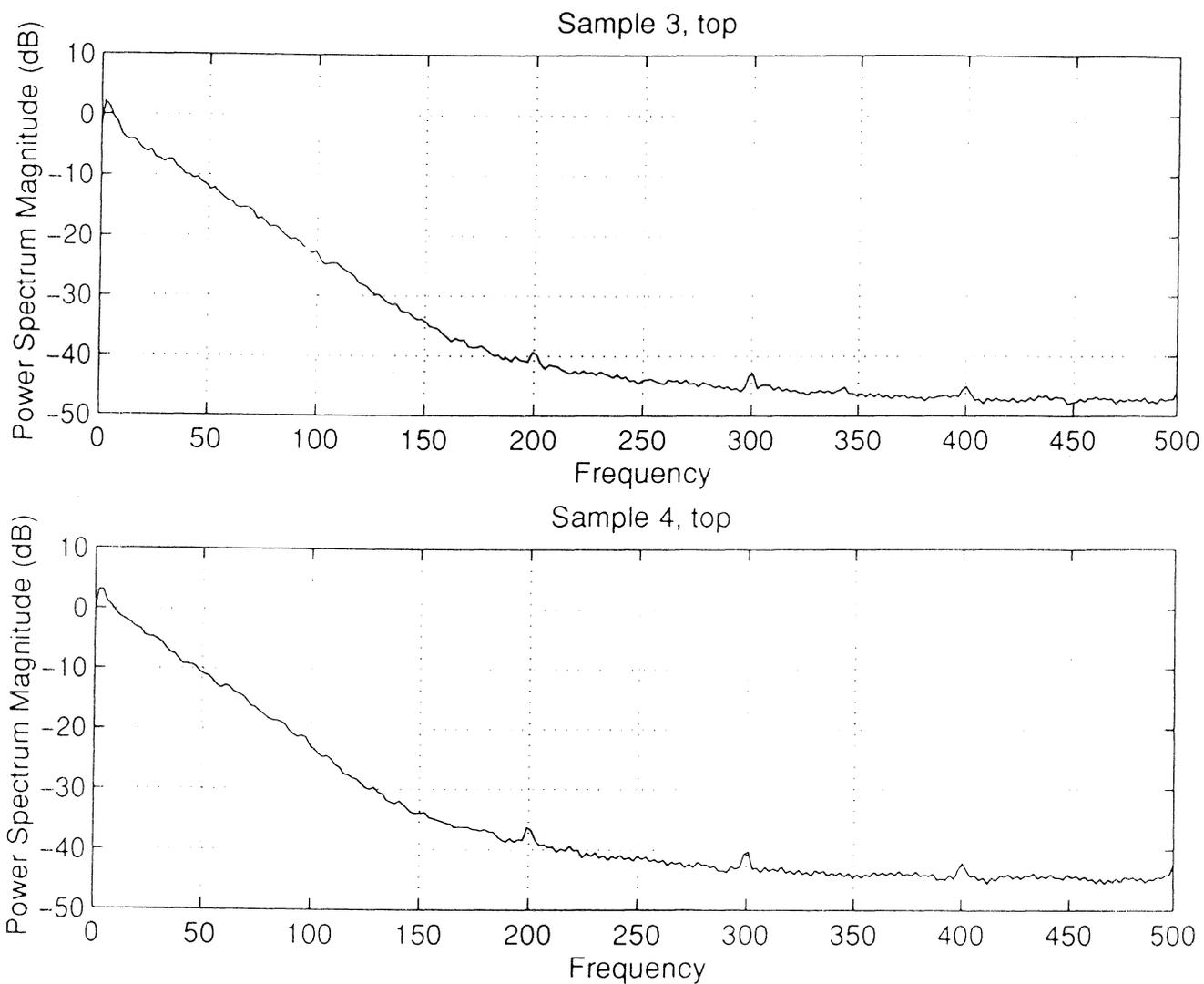
Fig. 9.2 Power spectra of the signal recordings made on the top sides of samples 3 and 4.
The frequency is given in Hz. The somewhat larger magnitudes for the frequencies
200, 300 and 400 Hz are caused by the mains voltage.

Fig. 9.3-9.8 Signal recordings made on long strips from a newsprint mill.
The samples are listed in table 9.1. *PMT high voltage setting = 2.50.*

Sample 1, top
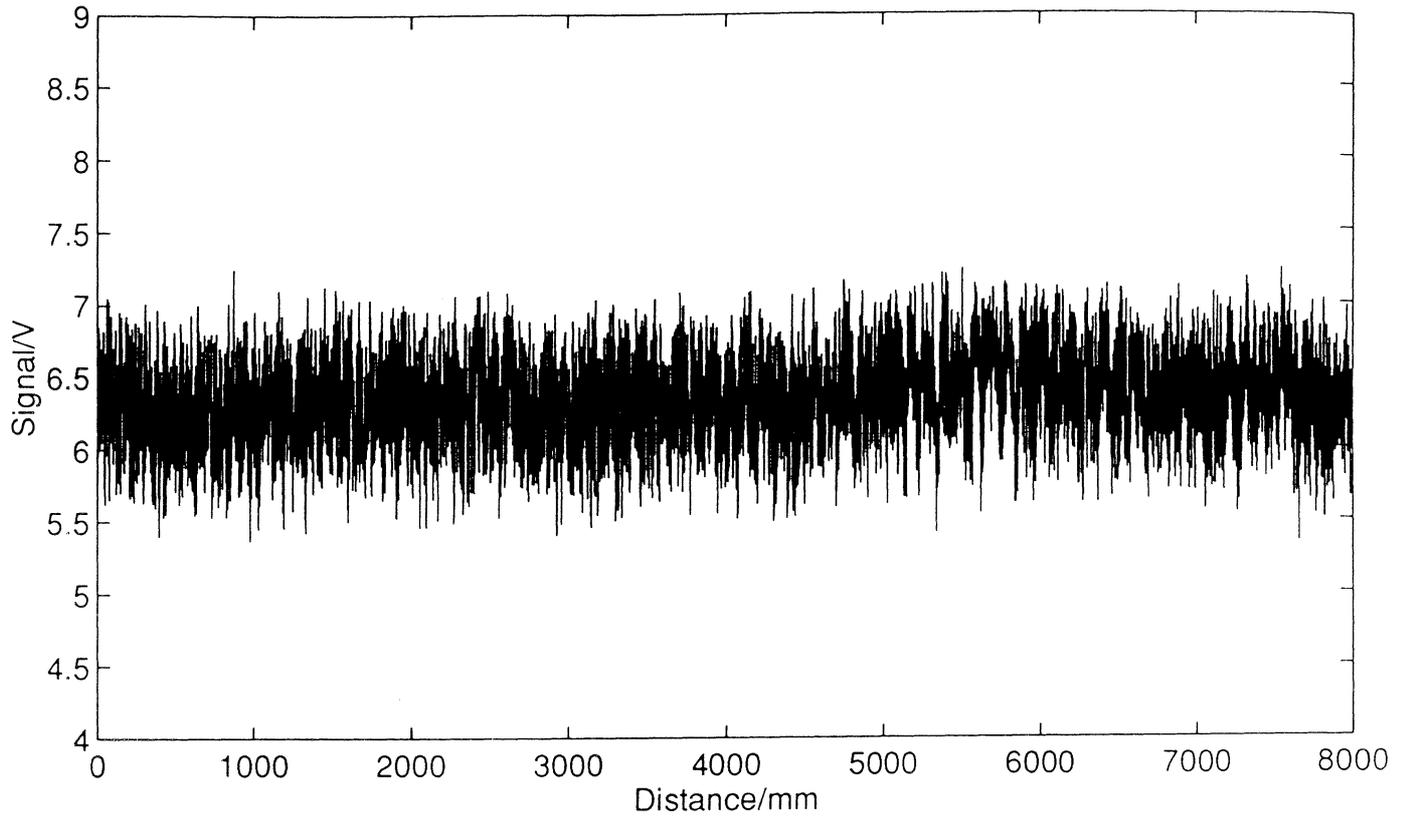
Sample 1, back
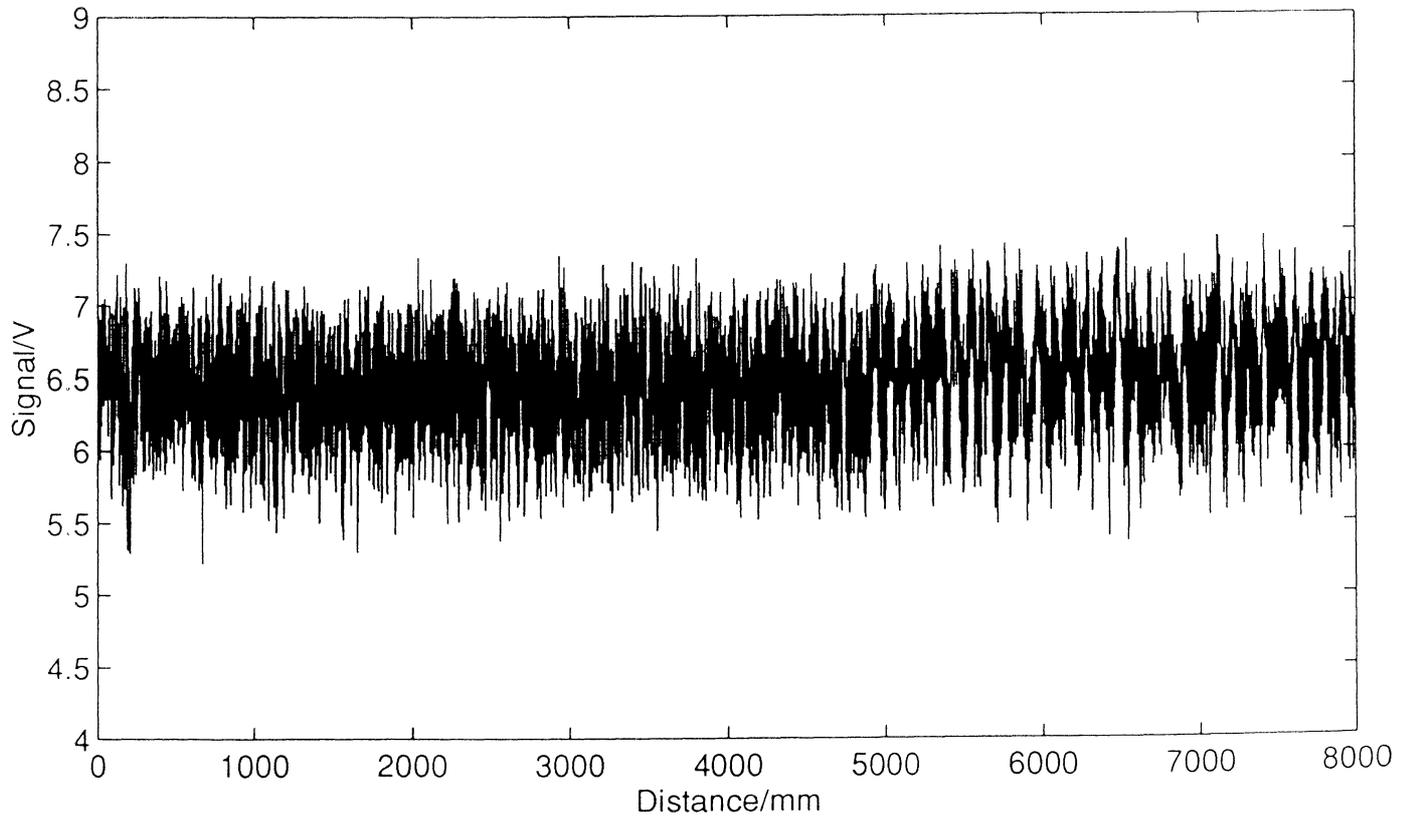
Sample 2, top
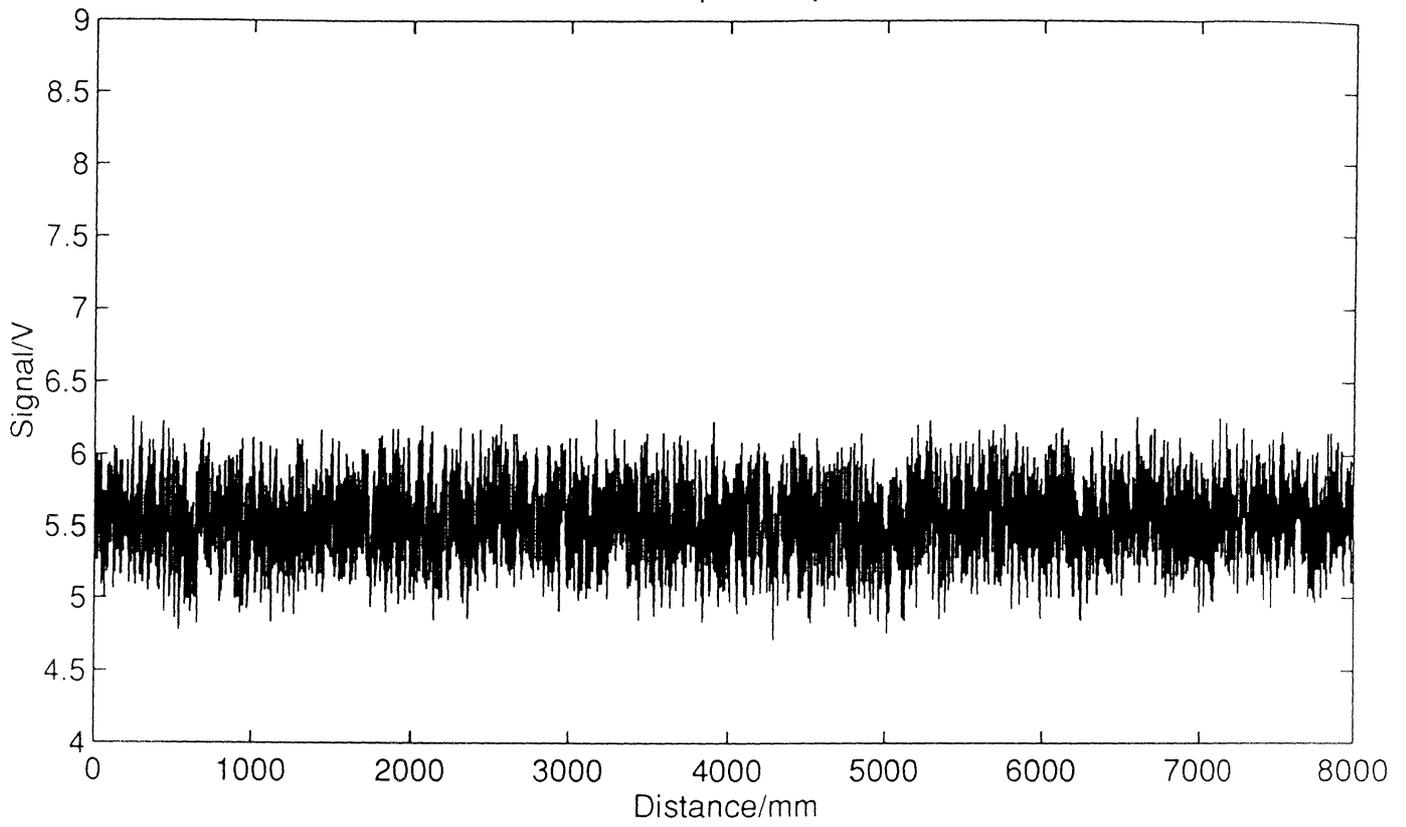
Sample 2, back
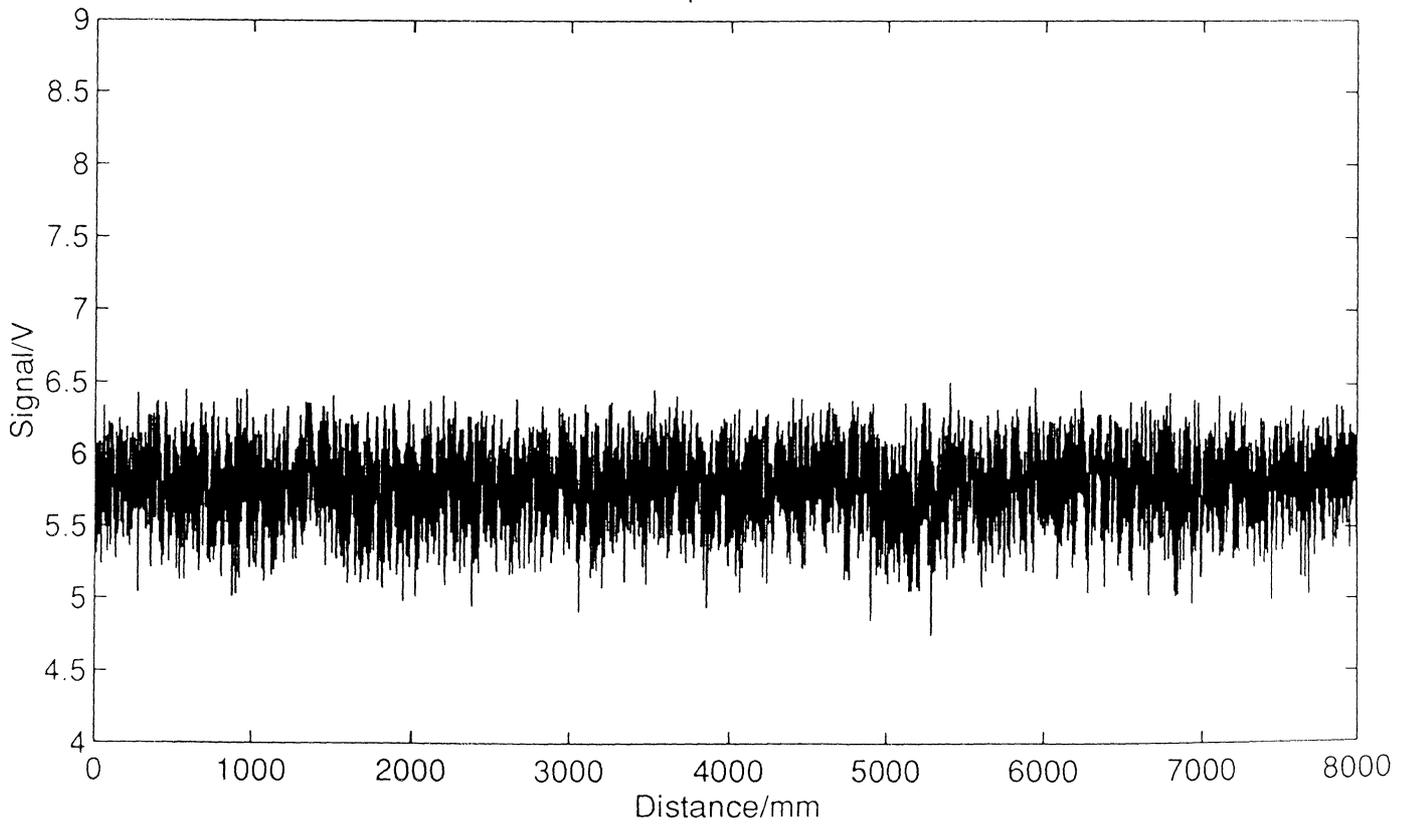
Sample 3, top

Sample 3, back

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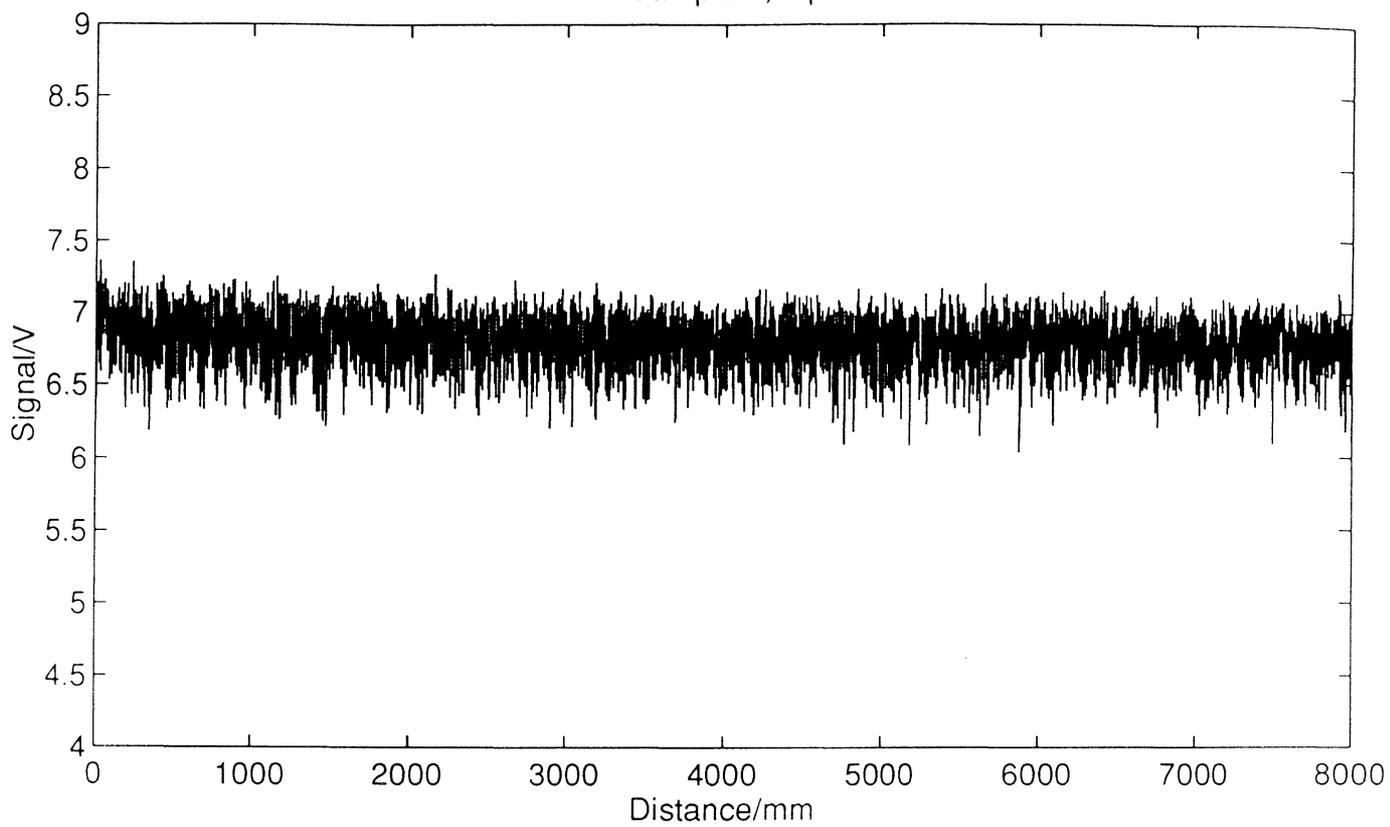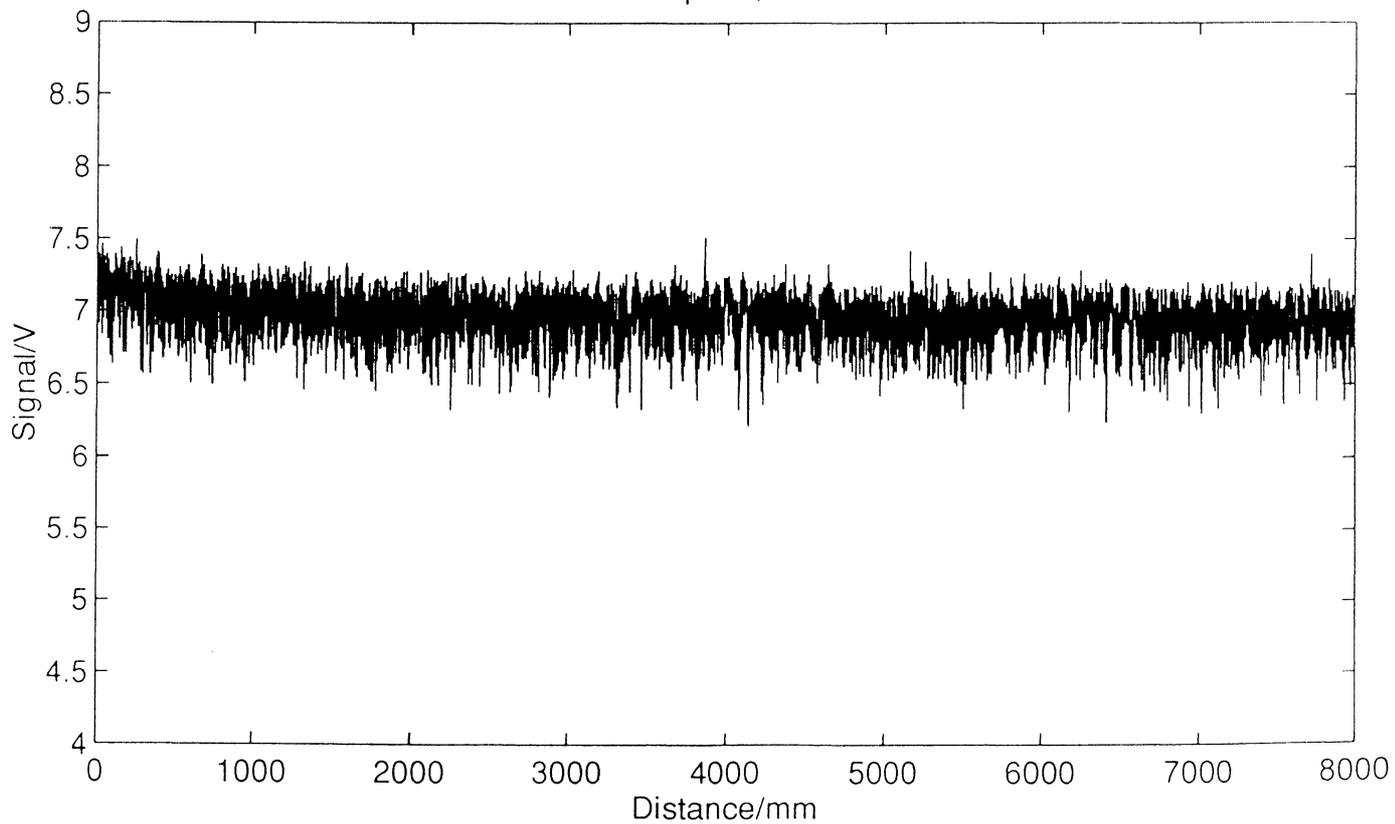
Sample 4, top
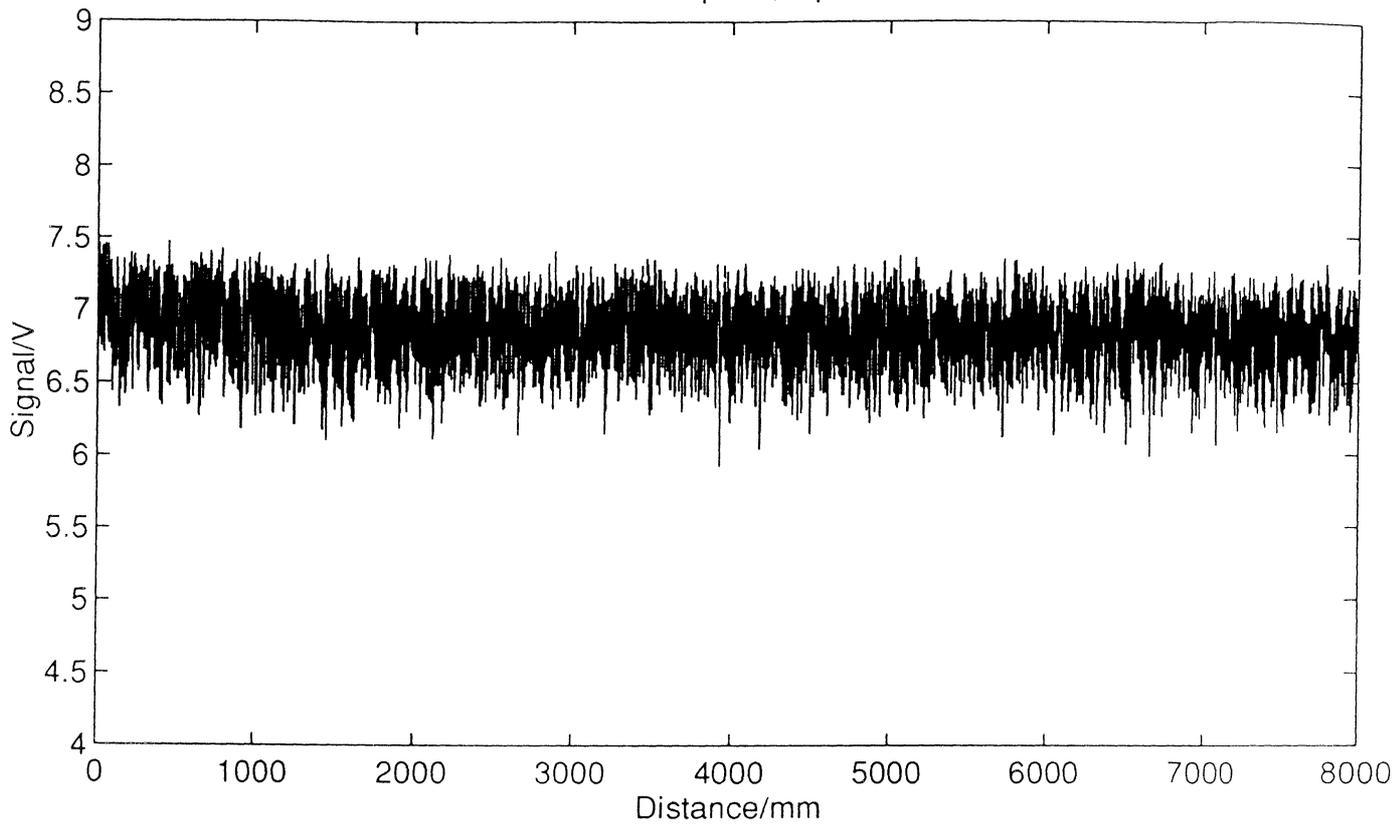
Sample 4, back
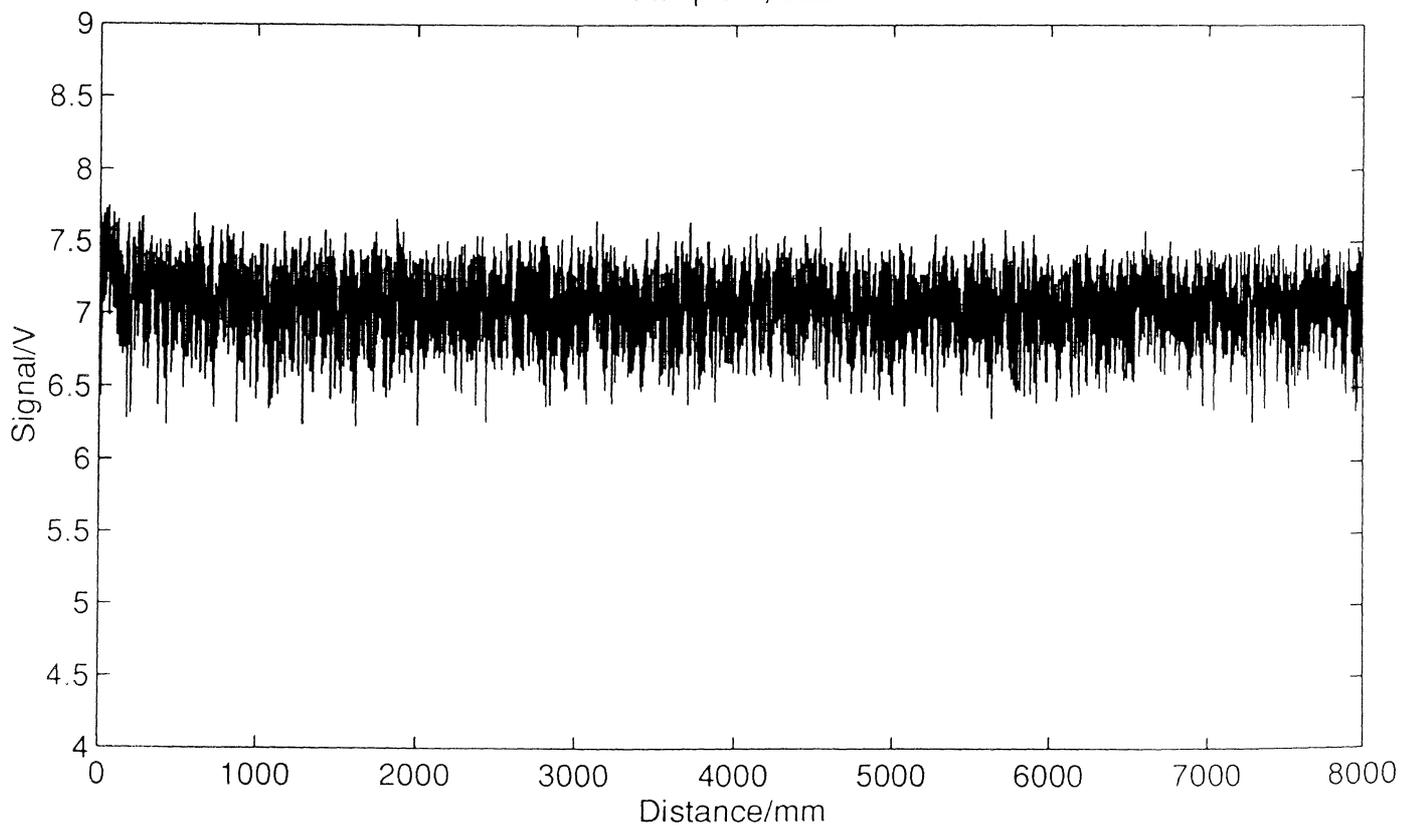
Sample 5, top
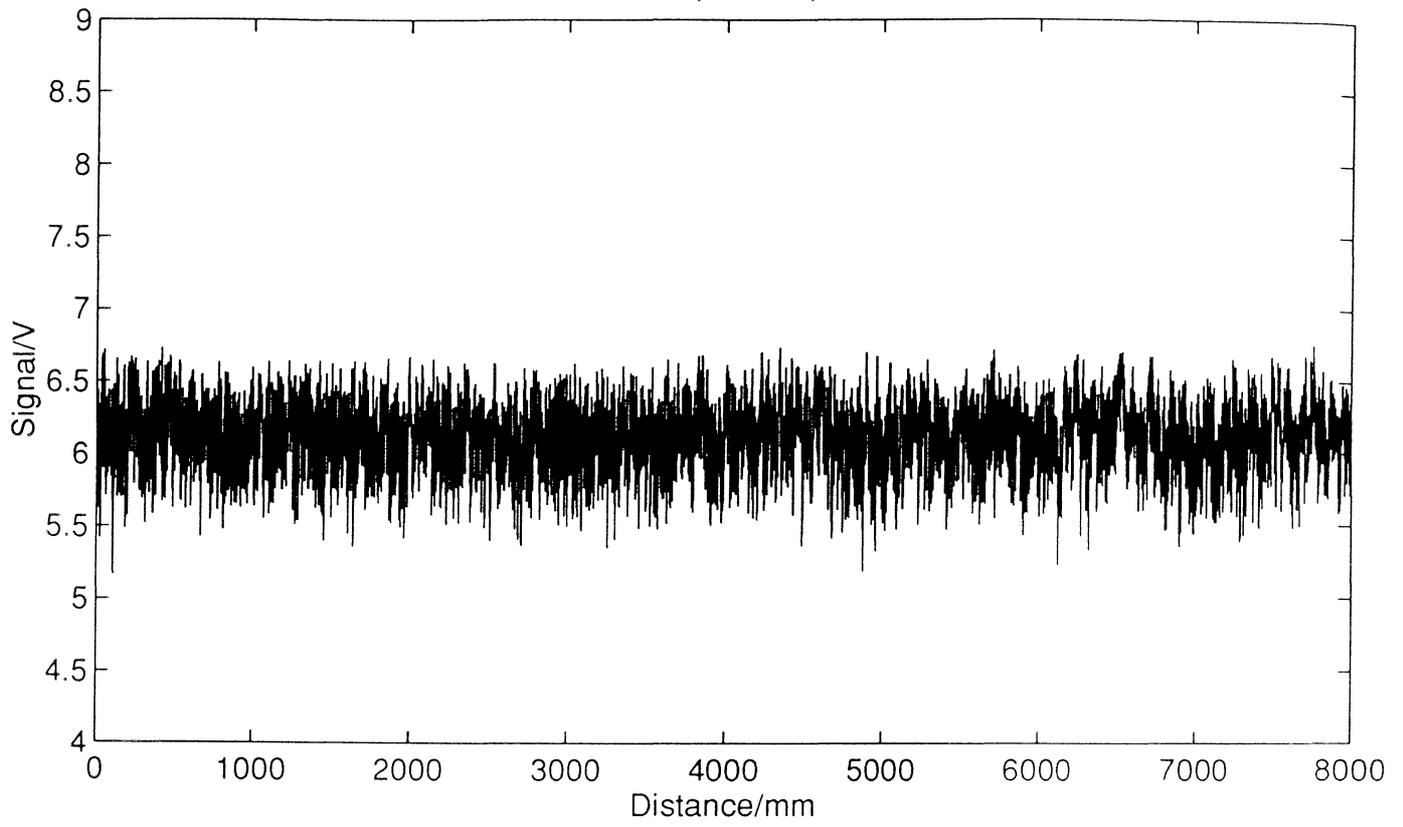
Sample 5, back
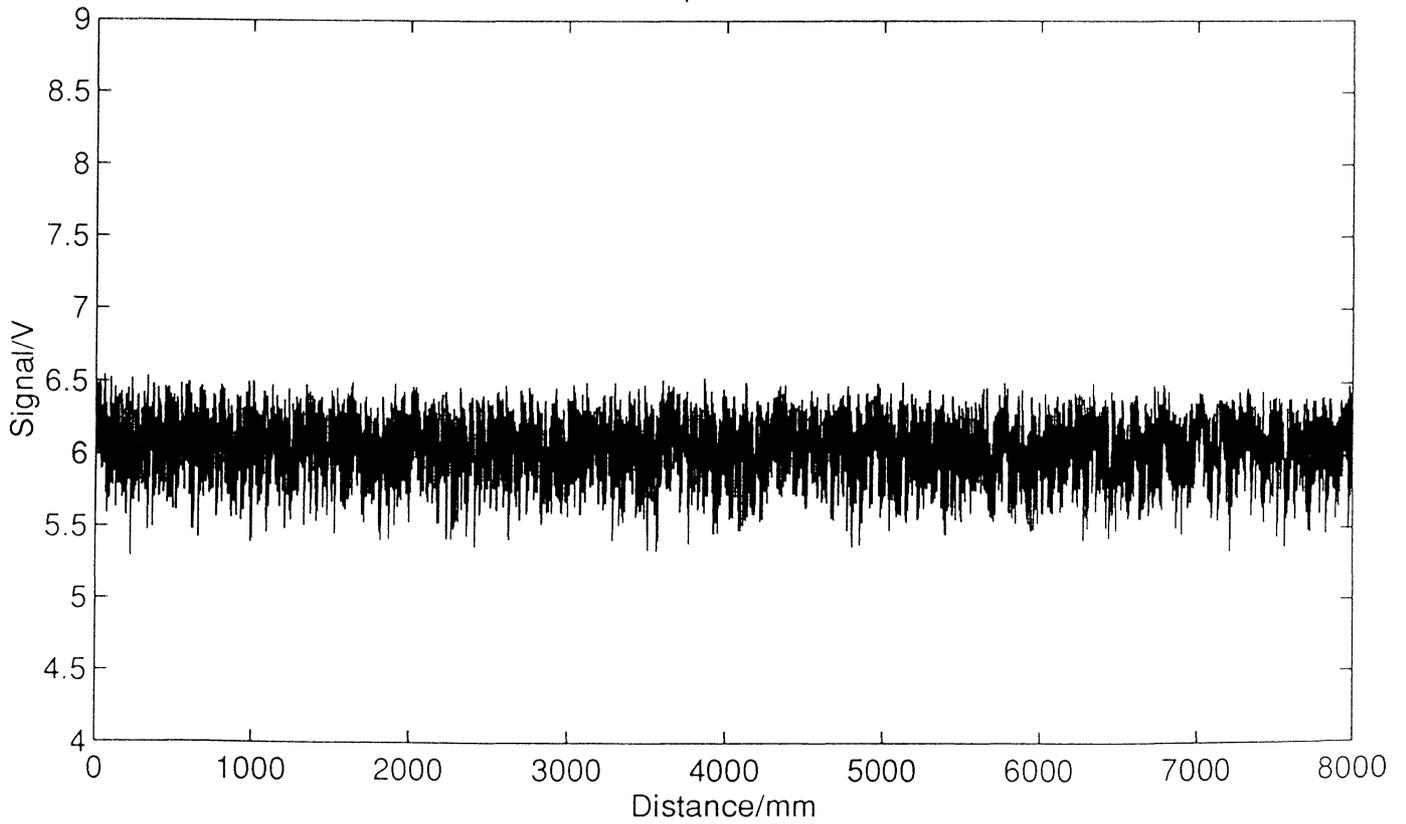
Sample 6, top
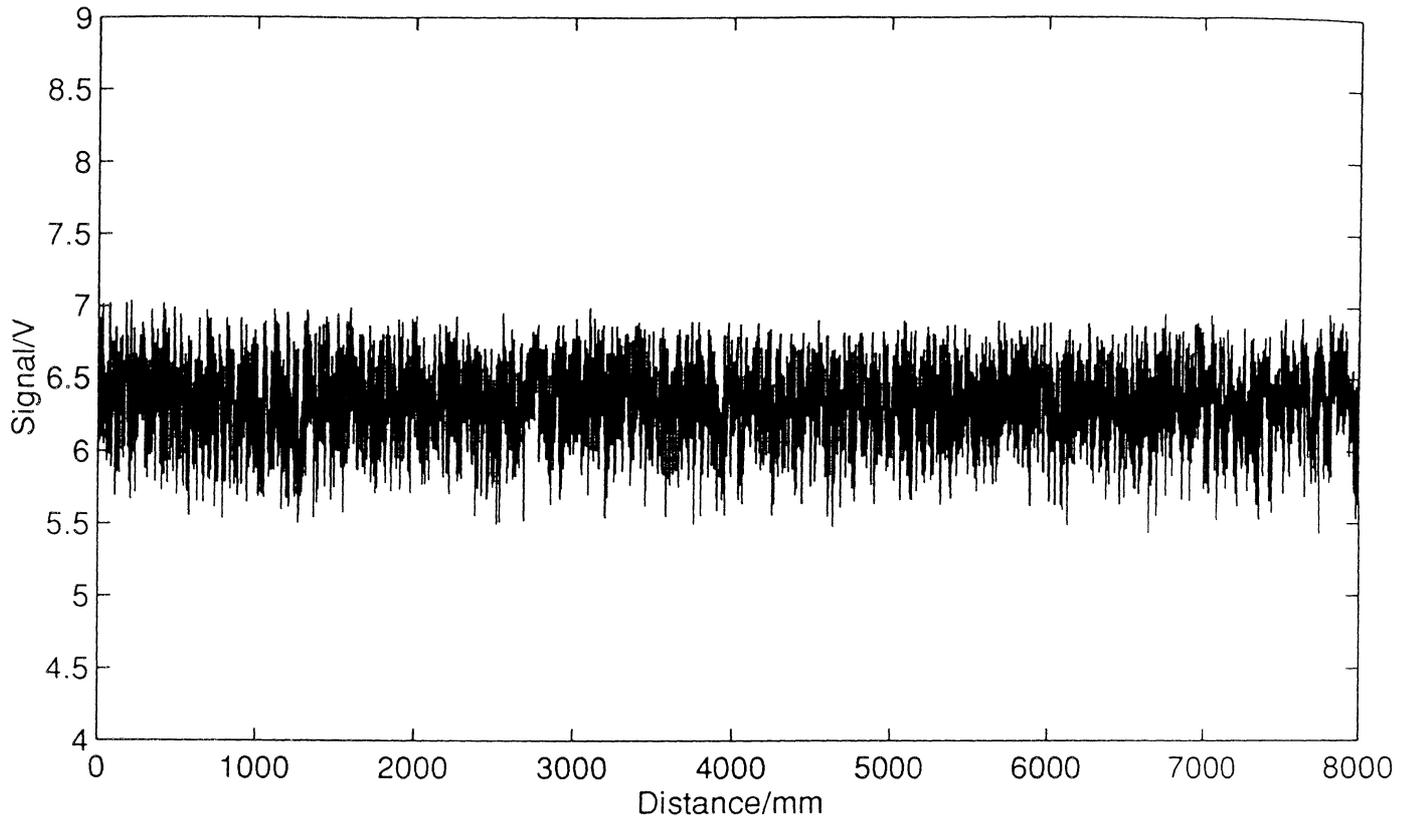
Sample 6, back
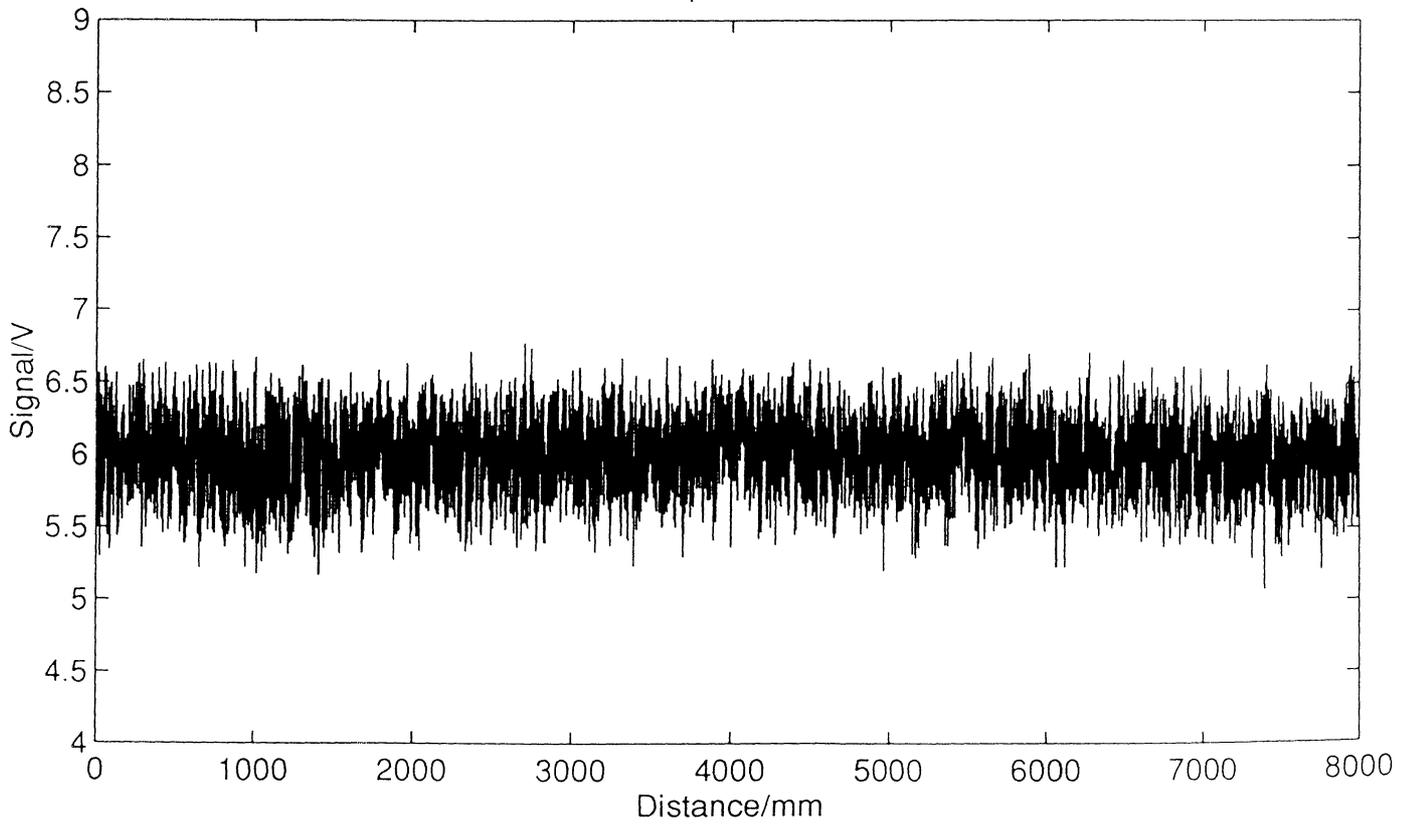
10 Conclusions

The tests and measurements performed have shown that the constructed equipment has a potential of being useful in future production monitoring. Its main advantages are the good linear response on the content of recycled fibre in newsprint (section 8.1.3), the highly reproducible signal (section 8.3) and its providing possibilities of performing well-resolved high-speed measurements.

However, besides the recycled fibre, the other constituents of the newsprint seem to influence the measured fluorescence intensity (section 8.2), not only in terms of their fluorescence. Also their absorption of fluorescence light and scattering of the excitation light may affect the measurements. Further investigations are needed in order to make clear what impact specific pulps and certain mixtures of them have on the measured signal. As for the influence of lignin, it can be compensated for by monitoring the lignin content (section 5.2) and the content of recycled fibre at the same time.

The good reproducibility ensures that the measured signal variations derive from systematic variations in the paper. Because of the weak background contribution (section 7.3.3) these are very likely to be variations in the fluorescence from the paper.

The spatial resolution obtained, corresponding to a light spot somewhat larger than 1 mm, was expected to be better (sections 7.1 and 7.3.7). The fact is, however, that no higher resolution is needed for real on-line situations, since the high web speed (some 20 m/s) of the paper machine results in a very large amount of data acquired per second.

The measurements performed on paper samples from production have pointed at some distribution differences occuring in the paper sheet. For instance the distribution of recycled fibre along a measured track may differ between the top and back sides of the sheet (section 8.3). Measurements on strips from a paper machine have indicated that the magnitude of the signal variations may differ between samples of different composition (section 9.2). Some samples also show smaller variations in the cross direction of the paper than in the machine direction.

The observations mentioned all indicate that distribution differences in the paper may be detected by the equipment. Future work should be directed towards investigations of how variations in the production conditions influence the distribution of recycled fibre and the measured fluorescence signal. Further, systems for the data acquisition and presentation in on-line industrial applications have to be developed.

Acknowledgements

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