PDA2000 Photometric Dispersion Analyser

Operating Manual

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Warranty

We guarantee the manufacture of the instrument and parts against faults for a period of twelve months from the invoice date.

If a fault should occur within this period then we undertake to either:

- Supply free of charge replacement parts for you to fit to the instrument.
- Upon return of the item at your expense, repair or replace (at our discretion) the instrument free of charge and return it to you at our expense.

1. Getting Started

Thank you for purchasing Rank Brothers equipment. Please ensure that you have read and understood this operating manual before use. Store this manual in a safe place for future reference.

1.1 Do Not

- Do not plug into your local mains supply until you have checked that your local supply voltage matches that stated on the label at the rear of the instrument (adjacent to the mains inlet connector).
- Do not change the fuse or remove any covers while the mains inlet lead is connected to the unit.

1.2 Do

- Do ensure that if the moulded plug is removed from the mains inlet lead it is disposed of safely.
- Do read and understand this manual before use.

1.3 Connection to your Mains Supply

IMPORTANT: This unit must be earthed to ensure operator safety. The mains inlet lead may have a moulded plug fitted that is not suitable for connection to your local supply. If it is necessary to remove this plug and fit a suitable one, the removed plug must be safely disposed. The removed plug would present a serious shock hazard if plugged into a suitable supply with the bare wires exposed.

The wires of the mains inlet lead are coloured as follows:

GREEN and YELLOW	EARTH
BLUE	NEUTRAL
BROWN	LIVE

As the colours of the wires in the mains lead may not correspond with the coloured markings identifying the connections in your plug, proceed as follows:

- The wire coloured GREEN and YELLOW must be connected to the terminal in the plug marked with the letter E or the earth symbol or coloured GREEN or coloured GREEN and YELLOW.
- The BLUE wire must be connected to the terminal marked N or coloured BLACK.
- The BROWN wire must be connected to the terminal marked L or coloured RED.

Before connecting the unit to your mains supply ensure that your supply voltage matches that on the label at the rear of the instrument (adjacent to the inlet connector).

For operator safety, only the correct fuse must be used. Before changing a fuse, switch off the mains supply and disconnect the mains inlet lead from the instrument. The correct fuse values are as follows:

220/240 V	T160mA
100/110 V	T315mA

The unit contains no user serviceable parts. The cover should be removed by competent personnel only, after first switching off the power supply and disconnecting the mains inlet lead.

For any servicing or repairs, the unit should be returned to the manufacturer with a covering letter. Please ensure the unit is carefully packaged to avoid damage during shipment.

2. Introducing the PDA2000

The Rank Brothers Photometric Dispersion Analyser, PDA2000, is intended as a monitor of flowing suspensions and emulsions, both in research laboratories and in industrial applications. It provides a sensitive indication of changes in the state of aggregation of a suspension, either aggregation (flocculation) or disaggregation (dispersion, de-flocculation). The formation and breakage of emulsions can also be monitored by the PDA2000, and is applicable over a wide range of suspension concentrations and particle sizes.

2.1 Theory of Operation

The basis of the technique is the fact that in any suspension or emulsion, however well mixed, there are small-scale, local fluctuations in composition. These fluctuations follow the well-known Poisson distribution, so that the standard deviation about the mean is the square root of the mean value. Thus, in a volume of suspension which contains on average 1000 particles, we might actually find 1015, 971, 993, 1025 etc. particles, the actual number varying randomly around 1000 with a standard deviation of about 32. 95% of samples examined should have a particle number within two standard deviations of the mean (i.e. 1000 ± 64). By choosing a smaller sample volume, containing only 100 particles on average, the standard deviation would be 10, so that the variations would be larger, relative to the mean value, than in the previous case. The smaller the average number of particles, the more noticeable the variations become.

The PDA2000 illuminates the flowing suspension by a narrow beam of light (from a high intensity light emitting diode) so that a small sample volume is examined (of the order of 1 mm^3). Since the suspension is flowing, the number of particles in the light beam is continuously changing because of local variations in composition. These variations cause fluctuations in the intensity of transmitted light. The light intensity is monitored by a sensitive photodiode, the output of which is converted to a voltage proportional to the

intensity. The output voltage has a large dc component corresponding to the average transmitted light intensity (related to the turbidity of the suspension) and a much smaller fluctuating (ac) component due to the random variations in particle number mentioned above.

The ac component is separated from the dc component and amplified by a factor of up to 100 (see Figure 1). In this way fluctuations of the order of 1 mV or less in a dc signal of 10 V can be analysed. The technique used in the PDA2000 is to derive the root mean square (rms) value of the fluctuating (ac) signal, which has been shown to be a sensitive indicator of the state of aggregation of the suspension (reference 1). The frequency of the fluctuating signal depends on the flow rate of the suspension and the width of the light beam (in this case about 1 mm). For typical flow rates, the frequency is in the range 20–500 Hz, and when the flow stops, the fluctuations cease.

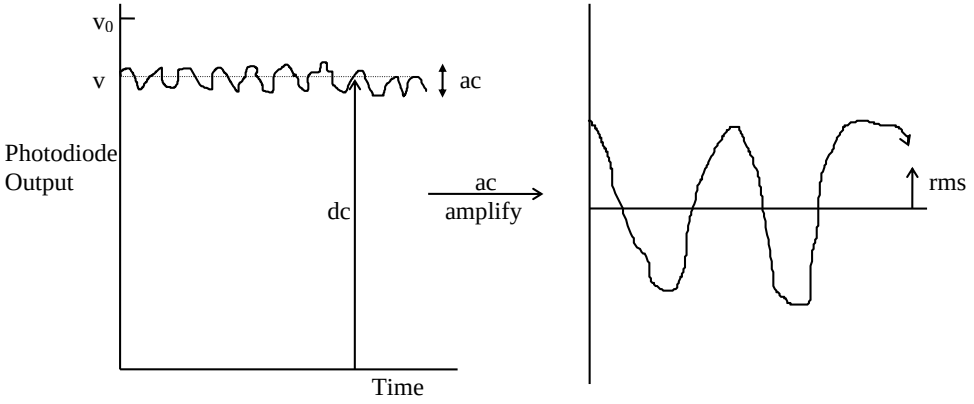

Figure 1 Processing of the photodiode output.

The rms value of the fluctuating signal depends on the concentration and size of the suspended particles (reference 2). For a uniform suspension, it is possible to estimate the particle number concentration (and hence the average size if the solids content is known). This requires knowledge of the turbidity of the suspension, which can be calculated from the dc value as explained in Appendix A. However, the most useful feature of the rms value is that it shows a marked increase as particles aggregate. Conversely, disaggregation causes a substantial decrease in the rms value. Corresponding changes in the dc value (or in the turbidity) are much less significant. In most practical cases quantitative interpretation of the rms reading in terms of particle or aggregate size distribution is not possible. Nevertheless, the reading gives a very useful empirical indication of the state of aggregation and enables optimum dosages of flocculants, dispersants and emulsifiers to be quickly established. Because of the flow-through nature of the technique, the PDA2000 could form the heart of an automated

laboratory test procedure and should find many applications in on-line monitoring and control of process streams.

3. Description of the PDA2000

3.1 Flow Cell

For the PDA2000, a novel flow cell has been developed which is most convenient for monitoring purposes. Transparent plastic tubing fits into a Perspex block which houses two precisely aligned fibre-optic probes. The optical fibres carry the incident light from a high intensity light-emitting diode (LED) and the transmitted light to a sensitive photodiode with a spectral response closely matched to the output of the LED (820 nm).

The flow cell accepts standard tubing of either 1 mm or 3 mm internal diameter, switching between these two being accomplished by simply changing a spacer between the fibre optic probes. Two spacers are supplied with the instrument, one for each size of tubing. The spacer not in use is held on the top of the Perspex block by a retaining screw. Spacers to accommodate other sizes of tubing (up to 5 mm ID) can be supplied to order. The right hand fibre optic probe is spring-loaded so that tubing can be removed and replaced very simply.

3.2 Signal Processing

The photodiode output goes to a pre-amplifier, the output of which is a voltage proportional to the intensity of light transmitted through the flowing suspension. The gain of the pre-amplifier may be set between 1 and 10 and the output is available either smoothed or unsmoothed. The pre-amplifier output is ac coupled to a second amplifier, the gain of which can be adjusted between 1 and 100. The output from this amplifier is a fluctuating signal that is available for display on an oscilloscope (at the Scope output). The fluctuating signal is passed to an rms-to-dc converter, the output of which is a voltage equal to the true rms value of the input signal. This rms voltage is available as an output on the PDA2000, either smoothed or unsmoothed. The rms value is divided by the dc voltage and the resulting ratio is available as another output, which is the most useful one for routine monitoring applications.

The limiter circuitry reduces effects caused by occasional air bubbles and non-representative large particles. It monitors the instantaneous value of the fluctuating signal and compares it with the average value for the last five seconds. Instantaneous readings exceeding 2.5 times the average are ignored and do not influence the rms reading.

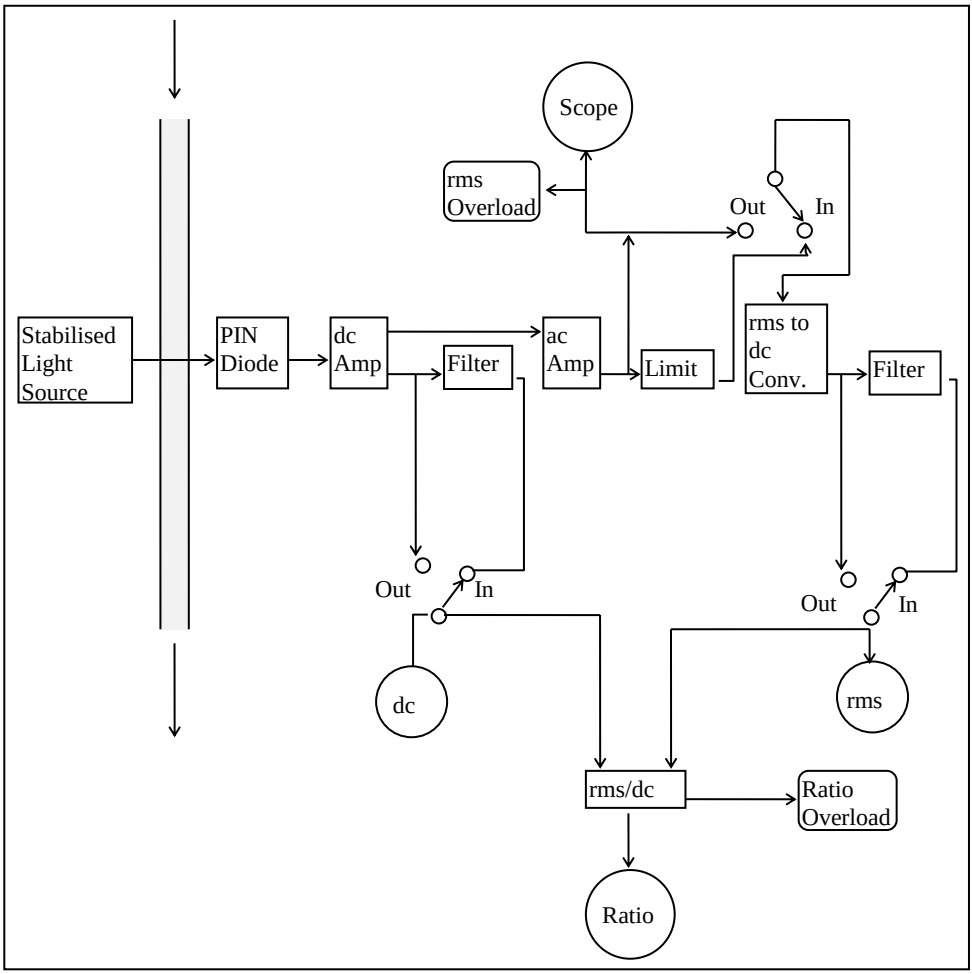

Figure 2 Schematic operation of the PDA2000.

3.3 Controls

3.3.1 Dc Gain

This control is a ten turn precision potentiometer and allows adjustment of the gain of the photodiode pre-amplifier over the range 1–10.

3.3.2 Rms Gain

This control is also a ten turn precision potentiometer and allows adjustment of the main ac amplifier gain between 5 and 500. The gain for a given setting is given by:

$$gain = 5 \times (1 + S/10)$$

Where S is the reading of the rms gain control. The full scale reading is 1000, thus if the rms gain control is set at 500 (half the full scale), the gain would be 5 × (1 + 50) = 255. Note the dc gain control has a direct effect on the fluctuating signal and hence this will change the rms output.

3.3.3 Rotary Switch

The rotary switch selects either the rms, dc, or ratio reading that will be displayed on the meter. These readings are all simultaneously available at the appropriate output sockets, regardless of the selector switch position.

3.3.3.1 Rms

This output gives the root mean square value of the amplified ac signal and the reading is affected by the dc gain and rms gain controls. Smoothing is available by depressing the Filter switch.

3.3.3.2 Ratio

This gives the ratio of the amplified rms and dc values, multiplied by 10 (i.e. ratio = 10 × (rms/dc)). The ratio will be affected by rms gain but not (within wide limits) by dc gain, which changes the dc and rms values by the same factor. Contamination of optical surfaces or drift in electronic components has almost no effect on the ratio output for similar reasons.

3.3.4 Limit

When this switch is depressed, the limiter circuitry is activated, considerably reducing the effects of large particles and air bubbles. The switch is illuminated blue when active.

3.3.5 Filter

This switch provides smoothing of the dc and rms output values (and hence also the ratio output). With the switch out, the averaging time applied to the output signals is 25 ms. With the *Filter* switch in, the averaging time is increased to 5 seconds, giving much smoother output traces. When rapid changes are being followed or when changes of the gain settings are required the filter should be switched off. The switch is illuminated blue when active.

3.4 Signal overload indicators

The two overload indicators are set above the appropriate rotary switch positions.

3.4.1 Rms Overload

If the peak voltage of the amplified ac signal exceeds about 10 volts or the rms value is greater than about 6 volts, then this overload lamp will light up. Under these conditions, the value at the rms output socket will be less than the true rms value of the ac signal. This condition can be corrected by reducing the setting of dc gain or rms gain, usually the latter. Even when the rms output value is quite low the rms overload lamp may flash occasionally. This is a result of the passage of unusually large particles, aggregates or air bubbles through the light beam and is of no great concern if the *Limit* switch is depressed.

3.4.2 Ratio Overload

The division circuitry in the PDA2000 has a limited dynamic range and is only linear if the rms output value is smaller than the dc output value (i.e. the ratio output is less than 10). If this condition is not met, then the *Ratio Overload* lamp will light up. When this happens the rms gain setting should be reduced.

3.5 Outputs

Four outputs are available on the front panel of the PDA2000. These are all low-impedance BNC sockets and enable required values to be displayed on a chart recorder, oscilloscope or other device. The maximum output level of any output is approximately 14 V. These outputs are all simultaneously available, regardless of the selector switch position.

3.5.1 Rms

This output gives the root mean square value of the amplified ac signal. The reading is affected by the *Dc Gain* and *Rms Gain* controls. The *Filter* switch allows smoothing of the signal.

3.5.2 Dc

This gives the output from the photodiode pre-amplifier and is a measure of the average transmitted light intensity. The magnitude is affected by the *Dc Gain* control. Operating the *Filter* switch may smooth the output signal.

3.5.3 Ratio

The ratio output gives an output equal to the rms reading divided by the dc signal multiplied by ten. This output is affected by the *Rms Gain* but not by the *Dc Gain*, the *Dc Gain* controlling both the ac and dc signal equally. The ratio output is also almost completely independent of electronic drift and contamination of the optical surfaces

3.5.4 Scope

The ac waveform, the magnitude of which is controlled by both the *Dc Gain* and *Rms Gain*, is available at this output for display on an oscilloscope. This gives a useful visual indication of the condition of the flowing suspension.

4. Operation

The PDA2000 should be allowed to warm up for about 10 minutes after switching on. Leads from the output sockets can be connected to appropriate devices (e.g. chart recorder, data logger, oscilloscope, etc.).

4.1 Choice of Tubing and Flow Rate

The flow cell will accept tubing of up to 5 mm internal diameter and the standard spacers supplied are for 1 mm or 3 mm tubes. The choice depends on the concentration (or turbidity) of the sample, the amount available and the nature of the aggregates (or flocs). For dilute, low turbidity suspensions, 3 mm tubing would give a better response because of the greater optical path length. With concentrated suspensions there may be insufficient transmitted light if the 3 mm tubing is used, so that the 1 mm tubing would be chosen. However, there are also flow rate considerations that may affect the choice of tubing.

The nature of the ac coupling used in the PDA2000 means that the frequency of the fluctuating signal should not be lower than about 10 Hz, otherwise some of the signal will be lost and the rms output will be lower than the true rms value. To avoid this condition, the average velocity of the particles through the light beam should be about 5 cm/s or greater. This corresponds to flow-rates of about 2.5 ml/min in a 1 mm tube or about 20 ml/min in a 3 mm tube, for lower flow rates the rms value will be reduced. For routine monitoring purposes, where a constant flow rate is maintained, useful readings can be obtained, even though the flow rate is lower than those quoted above. Nevertheless, it is recommended that, wherever possible, flow rates at least as great as those given above should be used. The rms value should then be independent of flow rate.

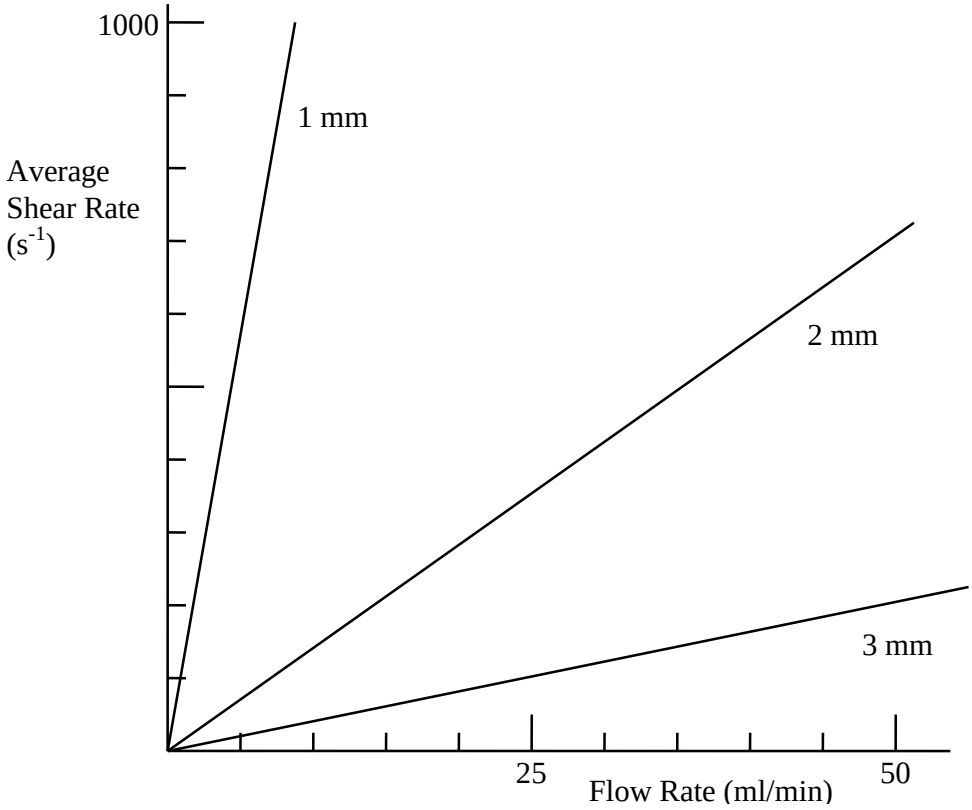

Figure 3 Average shear rate due to laminar flow in tubes of different diameters as a function of flow rate.

Another factor to be considered is the shear induced by laminar flow in tubes (see reference 3 and Appendix B). The average shear rate depends directly on the flow rate and inversely on the cube of the tube diameter. Figure 3 shows the way in which the shear varies with flow rate for tubes of 1 mm, 2 mm and 3 mm diameter. It is clear that in a 1 mm tube very high shear rates are attained, even at quite low flow rates. At the minimum flow rate suggested above (2.5 ml/min) the shear would be about 300 s^{-1}. It is likely that some aggregates would be disrupted at shear rates of a few hundred s^{-1}, which might be a limitation in using 1 mm tubing for a flocculation test. However, this effect could be exploited to give an empirical measure of floc strength, for instance by monitoring the rms or ratio output as the flow rate is increased. In tests of dispersion or emulsification the high shear rate in a 1 mm tube would assist these processes. In a 3 mm tube, shear rates are much lower and such effects would be less important.

In cases where flow rates of at least 20 ml/min can be maintained and where the suspensions are not very turbid, 3 mm tubing would usually be chosen. Reasons for choosing a 1 mm tube might be:

- High turbidity suspensions.
- Only small amounts of sample available.
- When high shear rates are required (e.g. in tests of floc strength or for dispersion monitoring).

A pump can induce flow but, wherever possible, gravity flow is recommended from a suitable constant head device. Peristaltic and similar pumps are likely to affect the readings since the flow does not remain constant, thus affecting rms readings.

4.2 Setting up the instrument

Having chosen the appropriate tubing ensure that the correct tubing spacer is in position. If not, rotate the spacer until the metal pin is in the groove and then move the spring-loaded fibre-optic probe as far as possible to the right. This will release the spacer so that it can be easily removed. Still keeping the probe in the same position, insert the correct spacer with its metal pin pointing forwards and then release the probe, which should then engage with the spacer.

Tubing is inserted in the groove of the tubing spacer, after moving the spring-loaded probe to the right. Releasing this probe should cause the tubing to be lightly gripped between the two probes. Check that the tube can be pulled through the cell with only light tension.

With suspensions that cause heavy contamination of the tube walls, it is best to use only a short length of tubing in the flow cell. This can be joined to tubing carrying the flowing suspension by suitable connectors and replaced as often as necessary. Where contamination is not a serious problem, it is more convenient to use one continuous length of tubing.

Flow clean water (or any other dispersion medium) through the tube and turn the rotary switch to the dc position so that the dc reading is displayed. Adjust the *Dc Gain* control until the reading comes to some predetermined value, say 10 volts. Note this adjustment should be carried out with the *Filter* switched off. The dc reading will almost certainly change if the tubing is moved because of variations in the thickness and transmission of the tube walls. During a test, ensure that neither the tubing nor the probes are moved. If an incident dc reading (i.e. for clean liquid) of 10 volts cannot be achieved even at maximum setting of dc gain, it is likely that there is some blockage of the light path. Check the reading without the tubing present and clean the faces of the fibre optic probes if necessary. A decrease in the incident reading will occur if the tube walls become coated with adhering particles, but, provided that the reading can be adjusted

to the required value by the *Dc Gain* control, this is of little concern. The tubing will need to be replaced when the required dc value cannot be obtained.

Note it is not advisable to adjust *Dc Gain* to give a dc reading of more than 10 volts, otherwise the dc amplifier will be approaching saturation, and give erroneous rms readings due to signal clipping.

With clean liquid flowing through the tubing, the rms and ratio readings should be very low. Because of the high sensitivity of the PDA2000, even 'pure' water may give a measurable rms value due to the presence of dust particles, bacteria, etc. For a dc reading of 10 volts, the rms reading at maximum gain might be about 100 mV (i.e. a reading of 0.10 volts on the display) depending on the purity of the water. Membrane filtration (0.4 micron) can substantially reduce the number of stray particles and the rms reading should then be noticeably lower. When the flow is stopped, the rms reading should in principle be zero, but in practice, a small value will usually be found due to intrinsic electronic noise in the instrument. For a dc reading of 10 volts the rms reading at maximum gain is usually around 20–30 mV for no-flow conditions. Since the maximum rms gain is 100, this noise level represents only about 50 µV in a dc value of 10 volts. For particle-free water, the rms reading will be the same low value whether or not the water is flowing.

4.3 Response with Flowing Suspensions

When a suspension flows through the tube, the dc, rms and ratio outputs will all be affected. The presence of particles in the light beam causes the dc reading to be reduced because of scattering and absorption of light by the particles. The dc reading together with the incident value can be used to calculate the turbidity of the suspension (see Appendix A). Usually the flow has very little effect on the turbidity, except for highly anisotropic particles, which may be aligned by the flow.

The rms reading for a flowing suspension depends on the concentration, nature and size of the suspended particles. At very low concentrations, the rms value increases as the square root of the particle concentration (reference 1) but at higher concentrations, the value passes through a maximum and then decreases. This is due to the increasing turbidity of the suspension and the maximum occurs when the dc value is about 60% of the incident value (i.e. when 60% of the light is transmitted). The ratio value (rms/dc) also increases as the square root of the particle concentration and this increase continues up to higher concentrations than for the rms value. Eventually, at high particle concentrations, this increase levels off and the ratio reading may pass through a maximum (reference 2). The behaviour of the dc, rms and ratio values with increasing particle concentration are shown schematically in Figure 4. This applies to suspensions where only the concentration is changing, with no change in the size or state of aggregation of the particles.

For a given weight concentration, the rms and ratio values depend very much on the size of the particles and their optical properties. It is not possible to give a precise idea of the values to be expected for particular suspensions. Generally, the rms and ratio readings will be greater for larger particles and for particles of a higher refractive index. For similar reasons, it is difficult to quote precise limits of particle size and concentration that can be monitored by the PDA2000. Particles with a size greater than about 2 microns should be detectable at concentrations down to 1 ppm or lower using the 3 mm tubing. Smaller particles should be detectable at somewhat higher concentrations and the minimum detectable size will be about 0.5 micron. For a suspension with a distribution of particle sizes, the larger particles give the dominant contribution to rms and ratio values.

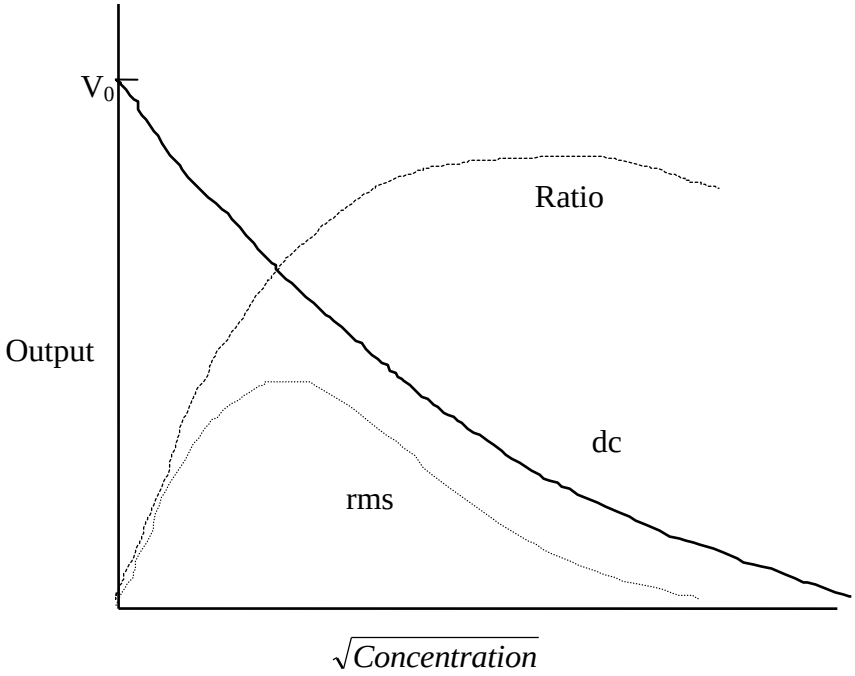

Figure 4 Response of PDA2000 outputs to increasing concentration.

The upper limit of suspension concentration depends on the turbidity and the optical path length. With 1 mm tubing, suspensions of up to a few percent solids can be directly monitored. For more concentrated suspensions some dilution will be necessary. With concentrated suspensions, the dc output becomes very low and it may be worthwhile to increase dc gain to its maximum value. In this way, the ratio output may still give useful empirical information on concentrated suspensions.

For a given suspension, changes in the state of aggregation of particles give large changes in the rms and ratio values and this is the most useful feature of the PDA2000. If the suspension is initially well dispersed, flocculation can cause an increase by a factor of five or more in these readings before any visible signs of change are apparent. During this increase, the dc output (and the turbidity) usually shows a change of only a few percent. When aggregates (flocs) have become quite large (say 0.2 mm), the rms and ratio readings show little further increase and may become rather erratic, even with the *Filter* and *Limit* switches in. This behaviour arises when the floc size is comparable with the width of the light beam (1 mm) and the flocs are relatively few in number.

When aggregates are disrupted, either by the addition of dispersing agents or the application of shear, the rms and ratio readings show a substantial decrease and reach a minimum value when the particles are fully dispersed. Again, changes by a factor of five or more can be expected if the initial suspension is highly aggregated. Transition from a slightly aggregated to a fully dispersed condition gives a smaller decrease, but can still be easily followed by the PDA2000.

The interpretation of changes in the ratio output in terms of aggregation or disaggregation of particles can only be made if the suspension concentration remains constant. However, the value changes, at most, as the square root of the solids concentration (see Figure 4). For instance, a doubling of the ratio value, which could occur with only a moderate degree of aggregation, would require at least a four-fold increase in the solids concentration with no aggregation. This would cause an appreciable increase in turbidity and hence a decrease in the dc output. Aggregation of particles causes only a slight change, usually an increase in the dc value. Therefore, if a significant increase in the ratio output occurs, with little change in the dc output, this is a clear indication that aggregation has occurred, rather than an increase in solids content. In the same way, a decrease in the ratio output clearly indicates disaggregation or dispersion, unless there is also a significant increase in the dc value.

In practice, there is little difficulty in interpreting the readings from the PDA2000. The table below summarises the important points. The extent of increase (+) and decrease (−) are roughly indicated by the number of the appropriate symbols.

	Effect of Response	
	Ratio Output	dc Output
Aggregation	+ + +	+ (−)
Disaggregation	− − −	− (+)
Increasing Solids	+	− −
Decreasing Solids	−	+ +

More information on the response of the instrument is given in Appendix A.

4.4 Monitoring

For routine monitoring applications, the ratio output is the most useful. This varies in a straightforward manner with suspension concentration (see Figure 4) and responds to changes in the state of aggregation in much the same way as the rms output. The main advantage of the ratio value is that it is almost entirely unaffected by contamination of the tube walls in the flow cell or by drift in electronic components. These effects cause the same proportional change in the dc and rms values, so that there is no change in the ratio output. For a given suspension, the ratio value depends only on the setting of rms gain. Monitoring can be carried out for very long periods without the need for recalibration.

Very small changes in the state of aggregation of a suspension can lead to changes of several percent or more in the ratio output, which provides a very useful check on the day-to-day reproducibility of a dispersion procedure. A reading that is higher than expected for a fully dispersed suspension is a clear indication of the presence of residual aggregates.

The easiest way of carrying out a laboratory dispersion or emulsification test is to dose increasing amounts of additive (dispersant or emulsifier) into a stirred vessel containing the sample under test and to withdraw them via a length of suitable tubing directly to the flow cell. If the tube length is kept short and the flow rate is at least the value recommended earlier (20 ml/min for a 3 mm tube, 2.5 ml/min for a 1 mm tube) then a response from the PDA2000 will be obtained within seconds of a change occurring in the stirred vessel. With this simple set-up the effects of stirring rate and of different types and concentrations of additives can be rapidly investigated.

A similar arrangement can be used to study flocculation in a stirred vessel. For dilute suspensions, flocculation may be quite slow and a long period of stirring may be required before flocs have grown to a sufficient size to settle at an appreciable rate. In the standard jar test procedure, widely used in water treatment applications, the turbidity of the supernatant water, after settling of flocs, is determined. The high sensitivity of the PDA2000 means that flocculation can be detected at a much earlier stage, long before visible flocs have formed. By measuring the ratio output at a fixed time after dosing (up to two minutes for dilute suspensions) it is possible to establish optimum dosages (by the maximum ratio) and to compare the effects of different flocculants. Break-up of flocs at high stirring rates may occur and this is immediately apparent as a decrease in the ratio output, so that comparisons of floc strength can be made.

Tube flow can form the basis of a convenient flocculation test (see Appendix B) and the PDA2000 is an ideal monitor for this purpose. The suspension is dosed with flocculant (from a variable speed dosing pump) in a small mixing vessel and the dosed suspension flows through a length of coiled tubing, where flocs may form, and then through the flow cell. Again, the optimum flocculant dosage is that giving the highest ratio reading.

In flocculation testing, the setting of rms gain should be low, so that the dispersed suspension gives a ratio reading of about 0.5. When flocculation occurs the reading may well rise to three or more. With a higher rms gain setting, flocculation might cause the *Rms Overload* lamp to light and the readings would not then be so reliable. When very large flocs form (≥ 0.2 mm) the response of the PDA2000 becomes rather erratic and it is better to avoid this condition. The instrument is much better suited to the early detection of the floc formation, rather than for measurements of large flocs.

As well as laboratory applications, the PDA2000 can be used as a monitor of process streams in a wide variety of industries. A sample can be continuously withdrawn at some convenient point and passed directly to the flow cell of the PDA2000, often by one continuous length of tubing using gravity flow. This gives a very simple, on-line method of monitoring the condition of suspensions and emulsions. It is not difficult to envisage cases where the ratio output could be used to control, for instance, the speed of a dosing pump, and hence to optimise the dosage.

4.5 Summary of Operating Procedure

1. Switch on the PDA2000 and allow it to warm up for at least 10 minutes.
2. Connect leads (e.g. to recorders, etc.).
3. Insert appropriate tubing (1 mm or 3 mm ID) having ensured that the correct spacer is in position.
4. With clean liquid in the tube, adjust *Dc Gain* until the dc output reaches some predetermined value (normally 10 volts). This adjustment should be carried out with the *Filter* switched off.
5. Flow suspension under test through the tube. The flow rate should preferably be at least 2.5 ml/min (1 mm tube) or 20 ml/min (3 mm tube).
6. Note the dc reading. If this is less than about 5% of the incident value (i.e. less than 0.5 V if 10 V was set in step 4) the suspension is too turbid for reliable monitoring. If possible, select narrower tubing and return to step 3. Alternatively, the *Dc Gain* setting can be increased to its maximum value. If this gives an acceptable dc reading (say greater than 0.5 V) then monitoring of the ratio output may still give useful information. Otherwise the suspension will need to be diluted.
7. Adjust *Rms Gain* to bring the ratio output to a suitable value. In a flocculation test, the ratio value for the dispersed suspension needs to be set low (less than 1) to avoid overload conditions as flocculation occurs. For dispersion testing, *Rms Gain* can be set high so that the ratio reading for the fully dispersed sample can be reliably monitored.
8. Monitor the ratio and dc outputs to follow changes in the suspension. (Note: for very turbid suspensions, the rms and dc values may be such that the *Ratio Overload* lamp lights up. In such cases decreasing the *Rms Gain* may give unsatisfactory results and the rms output should be monitored rather than ratio.)

5. Specifications

After 10-minute warm-up time, where appropriate.

	PDA2000
Power Requirements	110/120 V; 50/60 Hz; 13 W
	220/240 V; 50/60 Hz; 15 W
Size	380 mm (w) × 200 mm (d) × 140 mm (h)
Weight	4.5 kg
Temperature Range	5–40 °C
Light Source	LED 850 nm
Photodetector	PIN Photodiode
Frequency Range	6–2000 Hz
Outputs	BNC low impedance 0–12 V approx.
Display	LED, 0–19.99 V 0.1% ±1 count FSD
Filter Time Constant	5 seconds
Dc Gain	1–10 precision 10-turn
Rms Gain	5–500 precision 10-turn (±2%)
Ratio	±5% over full range

6. References

1. Gregory and D.W. Nelson, "A new optical method for flocculation monitoring" In Solid-Liquid Separation (J. Gregory, Ed.) Ellis Horwood, Chichester, 1984, pp. 172–182.
2. Gregory, "Turbidity fluctuations in flowing suspensions", J. Colloid Interface Sci., 105 (1985), pp. 357–371.
3. Gregory, "Flocculation in laminar tube flow", Chem. Eng. Sci. 36 (1981), pp. 1789–1794.

7. Appendix A: Turbidity Fluctuations

As outlined in the introduction, the basis of the technique used in the PDA2000 lies in the fundamental non-uniformity of suspensions and emulsions, when examined on a sufficiently small scale. In a flowing sample, local variations in composition can be made apparent as fluctuations in intensity of a narrow beam of transmitted light, or in other words, fluctuations in turbidity.

The turbidity of a suspension depends on the concentration and light scattering properties of the particles. If there are N identical particles per unit volume and their scattering cross-section is C, the intensity of a beam of light passing through a length L of the suspension is given by:

$$I = I_0 \cdot exp(-N \cdot C \cdot L) \qquad (A1)$$

Where I_0 is the incident intensity (i.e. the intensity of light transmitted through the suspending medium in the absence of particles).

This equation is often referred to as the Beer-Lambert Law.

The turbidity, τ, is defined simply as:

$$\tau = N \cdot C = (1 / L) \cdot ln(I_0 / I) \qquad (A2)$$

So that the Beer-Lambert Law, equation A1, may be written in the alternative form:

$$I / I_0 = V / V_0 = exp(-\tau \cdot L) \qquad (A3)$$

Where the term V / V_0 has been introduced since in practice, light intensities are often measured as voltage outputs from a suitable photodetector. V_0 is the voltage corresponding to the incident light intensity and V is the voltage when there are suspended particles in the light beam.

For non-uniform suspensions, containing N_1 particles per unit volume with scattering cross-section C_1, N_2 with C_2 etc., the turbidity is given by:

$$\tau = \Sigma N_i \cdot C_i \qquad (A4)$$

Where the sum is taken over all types of particle.

If the Beer-Lambert Law is obeyed, a plot of log(I) versus concentration should give a straight line. At very high concentrations departures from linearity occur because of multiple scattering effects, which cause the transmitted light intensity to be greater than that predicted by the Beer-Lambert Law. The turbidity of a suspension can be used to estimate the solids content if a calibration graph has been established for the same

material. However, changes in particle size, for instance by aggregation or disaggregation, can cause changes in the turbidity even though the solids content remains constant.

For very small particles (smaller than the wavelength of light used), aggregation causes an increase in turbidity, which can be used to follow the flocculation of sub-micron particles, although the change may not be great. For much larger particles, aggregation causes a decrease in turbidity because the amount of light scattered becomes proportional to the geometric cross-sectional area of the aggregate, which is less than the total cross-section of the individual particles. For intermediate particle sizes, turbidity is not a good guide to the state of aggregation.

For low-concentration suspensions, a significant change in turbidity can give a very small change in the transmitted light intensity. Thus for a suspension that transmits 98% of the incident light, halving the turbidity will give about 99% transmission or an increase of only about 1% in the light reaching the photodetector. Such small changes may be difficult to monitor reliably over long periods because of effects such as contamination of optical surfaces and drift in electronic components.

For a flowing suspension, fluctuations in turbidity can be observed as mentioned previously. Since the local variations in particle number concentration follow the Poisson distribution, the standard deviation about the mean is equal to the square root of the average number of particles in the sample volume (i.e. in the light beam). It can be shown fairly simply (reference 2) that the root mean square (rms) value of the fluctuations in transmitted light intensity depends on the square root of the particle concentration, the light scattering cross-section of the particles and the dimensions of the sample volume. The intensity fluctuations are measured as fluctuations in the output voltage from a photodetector. For a uniform suspension, the rms value of the voltage fluctuations V_{rms} is given by:

$$V_{rms} = V_0[exp(-N \cdot C \cdot L)] \cdot (N \cdot L / A)^{1/2} \cdot C \qquad (A5)$$

Where L is the optical path length (i.e. the internal diameter of the tubing used in the PDA2000) and A is the effective cross-sectional area of the light beam.

This equation shows why the rms value passes through a maximum at a certain particle concentration (see Figure 4). For very low concentration (low turbidity) suspensions, the exponential term in equation A5 is very close to unity and V_{rms} increases as the square root of the concentration. As the concentration is increased, the exponential term begins to decrease and eventually this term falls faster than the rise in $N^{1/2}$, giving an overall decrease in V_{rms}.

Combining equation A5 with the Beer-Lambert law, equation A3, gives:

$$V_{rms} / V = (N \cdot L / A)^{1/2} \cdot C \qquad (A6)$$

The term on the left-hand side of this equation is the ratio of rms value to the average dc value of the output voltage. This is equivalent to the ratio output available on the PDA2000 (after allowance is made for the setting of *Rms Gain*). Equation A6 indicates that the ratio value should increase indefinitely as the square root of the particle concentration and not pass through a maximum. In fact, departures from the Beer-Lambert law cause the ratio value to level off at high concentrations and it may even pass through a maximum and decrease slightly, as shown in Figure 4. The precise behaviour of the ratio value depends very much on the nature of the particles.

For non-uniform suspensions the ratio is given by:

$$V_{rms} / V = (L / A)^{1/2} \cdot (\Sigma N_i \cdot C_i^2)^{1/2} \qquad (A7)$$

Where the sum is taken over all types of particle (cf. equation A4).

The nature of the sum in equation A7 is such that the ratio is weighted heavily by the largest particles in a heteradispersed suspension.

When aggregation occurs in a suspension, the number of particles decreases and their average size increases. These changes have opposing effects on the rms value, but in virtually all cases of practical interest, the net effect is a substantial increase in V_{rms}. The same conclusion applies to the ratio value and for this reason the ratio output from the PDA2000 gives a very useful indication of the state of aggregation of a suspension, as discussed previously. It is not possible to derive quantitative information on, for instance, aggregate size distribution from the readings, since we have very little knowledge of the light scattering properties of real aggregates. Even if a suspension is initially monodispersed, aggregation soon causes a departure from this condition, giving a range of aggregate sizes. The larger aggregates have a predominant influence on the ratio value, which makes the response even more sensitive than simple calculations based on uniform suspensions (reference 1) suggest. For a similar reason the ratio value is a very good indicator of the effectiveness of a dispersion process, being especially sensitive to the presence of a few residual aggregates.

There is one special case where the PDA2000 can be used to derive useful quantitative information. For a suspension that is monodispersed (or nearly so), the outputs from the instrument can be combined to give the particle number concentration. For this purpose three values are needed:

1. The incident value of the output voltage V_0. This is just the dc output with clean water (or other suspending medium) in the flow cell.
2. The dc value when the suspension is flowing, V.

3. The ratio value, V_{rms} / V, this is obtained by dividing the ratio output by (10 × rms gain).

The first two of these enable the turbidity to be calculated from equation A3. Rearranging this slightly gives:

$$ln(V_0 / V) = N \cdot C \cdot L \qquad (A8)$$

Dividing through by equation A6 eliminates the scattering cross-section, C:

$$ln(V_0 / V) / (V_{rms} / V) = (N \cdot L \cdot A)^{1/2} \qquad (A9)$$

Now, L·A is the effective volume of the illuminated sample, so that N·L·A is the average number of particles in the sample volume (N is the number per unit volume). Thus, the term on the right hand side of equation A9 is the square root of the average number in the sample volume, which can be easily calculated since all of the quantities on the left hand side are measurable. If the sample volume is known (by calibration with a suspension of known number concentration), then the concentration of any other suspension can be determined from equation A9. This procedure requires no knowledge of the optical properties of the particles since the scattering cross-section was cancelled out in deriving equation A9.

As an example of this procedure, assume the following values:

$V_0 = 10.00$ volts (adjusted to this value by Dc Gain).

$V = 7.85$ volts (this is the dc output for the same setting of Dc Gain).

Ratio output = 1.75 for a scale reading of 300 on the Rms Gain control.

The actual value of rms gain (see above) is 5 × (1 + 30) = 155, so that the ratio value is:

$$V_{rms} / V = 1.75 / (10 \times 155) = 1.13 \times 10^{-3}$$

Substituting these values in equation A9:

$$(N \cdot L \cdot A)^{1/2} = ln(10 / 7.85) / (1.13 \times 10^{-3}) = 214$$

Therefore the average number of particles in the sample volume is $(214)^2 \approx 46000$. If the sample volume has been found to be 5×10^{-4} cm^3 (a typical value for a 1 mm tube), then the particle number concentration is given by:

$$N \approx 46000 / (5 \times 10^{-4}) \approx 9.2 \times 107 \ cm^{-3}$$

It should be stressed that this method is not applicable to heterodispersed suspensions, for which the number concentration calculated as above turns out to be considerably

less than the actual value (see reference 2). The expressions for such suspensions, equation A4 and equation A7, are such that division does not lead to a cancellation of the scattering cross-sections.

Nevertheless, there are many practical examples of nearly monodispersed suspensions (latex, blood cells, yeast cells, etc.), for which the simple procedure outlined above gives a rapid indication of number concentration. The results are more reliable for dilute suspensions, where the Beer-Lambert law is applicable, but even so, concentrations can be much higher than those necessary for more conventional particle counting techniques. The presence of aggregates can give misleading results. To determine the number of primary particles it is necessary to disrupt aggregates as far as possible, for instance by flow through a narrow tube (Appendix B).

8. Appendix B: Laminar Tube Flow

When a fluid flows at low speed through a straight tube of circular cross-section, there is a parabolic variation of velocity across the tube, first treated by Poiseuille. The velocity v_r at a radial distance r from the tube axis is given by:

$$v_r = v_0(l - r^2 / R^2) \qquad (B1)$$

Where R is the radius of the tube and v_0 is the maximum fluid velocity (at the tube axis). The velocity varies from zero at the tube wall to a maximum value at the axis. The average fluid velocity is half the maximum value.

Equation B1 only applies to laminar flow, where the Reynolds number is less than about 2000. For a 3 mm ID tube, the limiting flow rate is about 280 ml/min and for a 1 mm tube about 95 ml/min. It is unlikely that these flow rates would be exceeded in normal applications of the PDA2000, so we can assume laminar flow conditions.

The variation of velocity across the tube leads to a velocity gradient or shear rate, which also varies across the tube. At the tube axis, the shear rate is zero, since the fluid velocity has its maximum value there. The shear rate reaches a maximum value at the wall, where the fluid velocity changes most rapidly with radial distance. The average shear rate, G, is easily derived (reference 3) and can be expressed either in terms of the fluid velocity or the volumetric flow rate, Q:

$$G = 4v_0 / 3R = 8Q / 3\pi \cdot R^3 \qquad (B2)$$

The shear rate values in Figure 3 were calculated using equation B2.

In laboratory flocculation tests, it is often necessary to apply shear to a suspension in order to promote particle collisions (orthokinetic flocculation), especially with dilute suspensions, where Brownian motion is not sufficient to give aggregates (flocs) of the required size. If a shear rate G (seconds^{-1}) is applied for a time t (seconds), the amount of flocculation achieved is a function of the dimensionless number Gt (sometimes called the Camp number). A value of several thousand may be required, although this depends greatly on the suspension concentration and on the collision efficiency of the particles. If Brownian motion is insignificant, then, for a given Gt value, the extent of flocculation should be the same, whether a high shear rate is applied for a short time or vice versa. In laminar tube flow, the average shear rate is given by equation B2 and the average residence time in the tube depends on the flow rate and the tube volume:

$$t = \pi \cdot R^2 \cdot l / Q \qquad (B3)$$

Where l is the length of the tube.

Combining equation B2 and equation B3 gives:

$$Gt = 8l / 3R \qquad (B4)$$

This very simple result indicates that the Camp number, Gt, and hence the amount of flocculation, depend only on the dimensions of the tube and not on the flow rate. Although there are several respects in which this conclusion needs to be qualified (reference 3), it remains a very useful guide in the choice of suitable tube dimensions. If it has been established that a Gt value of 20,000 is needed, then nearly 4 metres of 1 mm tubing or more than 11 metres of 3 mm tubing would be required. When such lengths are needed, it is much more convenient to use coiled, rather than straight tubing. The effect of coiling is to introduce a secondary flow and some fluid mixing, which gives enhanced flocculation over that obtained with a straight tube of the same dimensions.

By increasing the flow rate through the tube the average shear rate is increased and this may decrease the particle collision efficiency or cause some break-up of existing flocs. In both cases a decrease in the ratio output from the PDA2000 would occur. Alternatively, flocs formed by flow in one tube might be disrupted when the suspension is made to flow through a narrower tube, again giving a measurable change in the ratio output. Thus the shear induced by tube flow can be exploited both to promote floc formation and to obtain information on the strength of flocs.

In dispersion testing, tube flow can be used as a reproducible means of applying shear to aggregates immediately before monitoring by the PDA2000. In narrow tubes, very high shear rates can be achieved at quite modest flow rates (see Figure 3). For estimating particle number concentrations (by the method outlined in Appendix A) a rate of flow through a 1 mm tube of around 20 ml/min or more would be sufficient to disrupt most aggregates, especially those of biological cells.

9. Appendix C: ADC-20 Data Logger Application Notes

9.1 General

It is important to follow the appropriate installation instructions for the logger. Please read the logger manual and these notes before proceeding any further.

The converter box allows connection of all four outputs from the PDA2000 to a data logger. It allows the connections to be made easily using BNC to 4 mm leads and is supplied with an interconnecting lead to the logger. The output voltages from the PDA2000 are reduced by a factor of 6 to ensure that the logger inputs are not overloaded. It is important that the voltages input to the 4 mm sockets on the rear of the converter box do not exceed 30 V dc otherwise the logger may be damaged. This voltage will not be exceeded when the converter box is used correctly with the PDA2000.

9.2 Software Installation

Before connecting the logger to your PC it is necessary to install the PicoLog software following any instructions supplied and selecting *ADC-20 / ADC-24* as the device. You can tick the *Install for other devices* option if you intend to use other Pico loggers on the PC, otherwise leave this unticked.

9.3 Connections

1. Ensure that the PDA2000 is switched off.
2. Connect the logger to the converter box using the 25-way lead supplied.
3. Connect the PDA2000 outputs to the converter box.
4. Connect the logger to your PC via a spare USB port. If this is the first time you have connected the logger then your PC will report *Found New Hardware*. Follow the on screen instructions to install the software drivers for the logger.

9.4 PicoLog Software

For further installation and operating information please read the PicoLog manual. To set up the software proceed as follows:

1. Run *PicoLog Recorder*.
2. In the *File* menu click *New settings*.
3. The *Recording* window should now open, ensure that the *Recording method* is *Real time continuous*, *Action at end of run* is *Stop*, *Restart delay* is *1 minute*, and *Use multiple converters* is unticked (these should be the default settings) then click *OK*.
4. The *Sampling Rate* window will now open. Adjust these to suit your experiment, leaving the *Readings per sample* set to *As many as possible*. This allows the logger to take readings as fast as possible and then average them over the sample interval to smooth out noise. Click *OK*.

5. The *Converter details* window now opens. The *Converter type* should default to that chosen at installation, if not then choose the appropriate device from the drop down window. In the *USB Devices* grid it should list your logger and its serial number (once the USB enumeration has completed). Click *OK*.
6. The *ADC-20 Channels* window will open showing the 8 channels available. Ensure that you select the correct *Mains Frequency* at the bottom to ensure best rejection of any mains related noise.
7. Now highlight *Channel 1* and click on *Edit*. In the *Edit ADC-20 Channel* window click in the *Name* box and rename this to *Rms*. The *Conversion Time* can be left at *60 ms* and in the *Voltage Range* box select *±2.500V.* The *Differential input enable* option **MUST BE TICKED**.
8. Click *Options…*, the *Parameter options* window opens. Tick *Use Parameter Formatting*, rename units to *V*, and adjust the *Number display* and *Scaling for graphs* as appropriate. (*Field width*: *4*, *Decimal places*: 2, *Minimum value*: *−2500*, *Maximum value*: *2500* should be suitable).
9. Click *Scaling*, and select *Equation* as the *Scaling method*. Set the scaling to *−X*6/1000* (this multiplies the reading by negative six and divides by one thousand to read in volts as per the PDA2000 display).
10. Click *OK* on each opened window until you return to the *ADC-20 Channels* window.
11. Repeat steps 7 to 10 for *Channel 3*, *Channel 5*, and *Channel 7*, renaming them *Dc*, *Ratio*, and *Scope* respectively. Note that channels 2, 4, 6 & 8 will be unavailable since they are used for differential input.
12. Click *OK* on the *ADC-20 Channels* window to return to the *PLW Recorder* window.
13. The *PLW Recorder* window displays the channels and their current readings. These should correspond closely to the readings on the PDA2000, however they are unlikely to be exactly the same. If the error is unacceptable, adjust the scaling as in step 9 above to correct the error. Note it is unlikely that you will be able to scale the readings to give exactly the same values as the PDA2000 over the entire output range.
14. In the *Settings* menu click *Sampling…* and adjust the number and interval of the readings to record, then click *OK*. A sample interval of 1 second and maximum of 500 readings is a good starting point.
15. From the *PLW Recorder* window click the *New file* icon in the top left of the window and enter a filename.
16. To start logging click on the *Start Recording* icon. To abort the recording click the *Stop recording* icon.
17. To view either a spreadsheet or a graph of the readings click on the appropriate icon at the top right of the window. Use the *Select channels* icon in the graph or spreadsheet window to select which channels are displayed.
18. When the recording has stopped, from the *PLW Spreadsheet* window click the *Select* icon to select the whole sheet, then click the *Write to disk* icon giving the file an

appropriate name. The file will be saved with a *prn* extension that can be opened in most spreadsheet programs to allow further processing of the data.

This information is correct for release 5.24.8 of the PicoLog software. Other features and facilities are available and further information is available in the PicoLog manual.

Note the Scope output on the PDA2000 is a raw data signal and is not ideal for the ADC-20 as it can only sample at a few samples per second.