Fluoroptic Solids Holdup Measurement in Slurry Systems

P. Huizenga, R. Meijer, J. A. M. Kuipers, and W. P. M. van Swaaij
Dept. of Chemical Engineering, Twente University of Technology, 7500 AE Enschede, The Netherlands

A large number of articles have appeared in literature discussing the determination of phase holdups in multiphase systems. For any multiphase system, by definition the sum of the holdups of the individual phases should equal one. This leads to the following expression for a three-phase system

$$\epsilon_S^{\#} + \epsilon_L^{\#} + \epsilon_G^{\#} = 1 \tag{1}$$

Furthermore, in three-phase systems the contributions of acceleration and friction to the axial pressure gradient can generally be neglected, leading to the well-known manometer formula

$$-\frac{dp}{dz} = (\rho_S \epsilon_S^{\#} + \rho_L \epsilon_L^{\#} + \rho_G \epsilon_G^{\#}) g \tag{2}$$

From Eq. 1, it follows that in theory one could determine solids holdup in three-phase systems by measuring the holdup of both the gas and the liquid phase. Another option would be measuring either of these holdups and the pressure gradient allowing calculation of the solids holdup from Eqs. 1 and 2. For the low solids holdups typically encountered in slurry reactors (< 15 vol. %) both approaches mentioned would, however, introduce considerable inaccuracies. Therefore, in slurry systems solids holdup should preferably be determined directly. A number of measurement techniques that could be considered for direct solids holdup determination in slurry systems will subsequently be briefly discussed together with their advantages and disadvantages.

Sampling

A liquid-solid sample withdrawn from a three-phase column can, for example, be analyzed by weighing it before and after drying. Although the accuracy of the sample analysis is high, the representativeness of the sample for the system from which it was taken should be checked carefully. Further weak points of this technique are its laboriousness and the hydrodynamic disturbance generated in the system studied. The robustness of the technique and its relatively easy implementation are its main strong points.

Electrical Conductivity

When applying this technique, the conductivities of the three-phase dispersion and the continuous phase alone are measured. For nonconducting particles, the ratio of the measured conductivities can then be related to the continuous- (liquid-) phase holdup (Begovich and Watson, 1978; Uribe-Salas et al., 1994). Direct solids holdup determination using this principle in gas-liquid-solid systems is, however, not possible.

Electromagnetic Permeability

The determination of phase holdups by measuring the permeability of a multiphase system to electromagnetic radiation has been applied frequently (see, for example, Lee and Worthington, 1974; Kuipers et al., 1992). The whole spectrum ranging from infrared (IR), visible (VIS) and ultraviolet (UV) light to X- and γ-radiation is covered. In three-phase systems the electromagnetic permeability depends on the holdups of all phases present. Therefore, generally, no single holdup can be determined accurately by measuring this quantity in three-phase systems. Exceptions occur when the two remaining phases are well mixed or possess almost equal permeabilities. In these rather uncommon cases the two remaining phases can be treated as if they were a single phase.

Ultrasonic Sound Wave Distortion

Uchida et al. (1989) established a principle for measuring gas, liquid and solids holdup simultaneously in a three-phase system by analyzing the shape and the phase lead or lag of an ultrasonic sound wave. An ultrasonic burst wave is transmitted into a medium that may be either a liquid or a multiphase system, and its response is subsequently detected. Solids generally have a higher transport velocity for sound waves than a liquid. Their presence, therefore, results in a phase lead as compared to the pure liquid response. In a

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Correspondence concerning this article should be addressed to P. Huizenga.

system also containing bubbles some parts of the sound wave are reflected. Other parts may travel in an unhindered manner, leading to the same signal as for a liquid-solid system. Finally, some parts of the wave may be accelerated due to bubble induced fluid motion resulting in an additional phase lead. From the envelope of all measured signals, holdups of the individual phases can be determined. As can be concluded from Figure 3 of Uchida et al. (1989), solids holdups up to 5 vol. % can be determined in their system with an accuracy of about 1 vol. %, which leads to a relative measurement error of 20% or more. The nonintrusive character of this technique and the absence of necessity to alter any phase constitute considerable advantages to this technique, with its inaccuracy being its main disadvantage.

Ferromagnetic Tracer Particles

The magnetic permeability of a cross-section of a system is measured by an inductance probe which is assumed to produce a signal output proportional to the amount of ferromagnetic solids present in that cross-section (Avidan, 1980). Ferrite or nickel is generally used to give ferromagnetic properties to the tracer material. The technique was applied in a three-phase system by Kafarov et al. (1973). To our knowledge, however, neither has the attainable accuracy of the technique been determined nor has the assumed proportionality between signal and solids holdup been proven.

Reflection Fiber Probe

An optical fiber reflection probe giving characteristic signals for both bubbles and particles in a three-phase fluidized bed was developed by Ishida and Tanaka (1982). Hu et al. (1986) applied this technique at solids concentrations ranging from 30 to 45 vol. %. According to Ishida and Tanaka (1982), particle dependent signal intensity became weak in the dispersed zone of their three-phase fluidized bed. Therefore, this technique will probably not work at the low solids holdups typically encountered in slurry bubble columns.

The techniques discussed are compared in Table 1. It can be concluded from this table and the foregoing discussion that, at present, except for sampling, no reliable direct techniques are available for solids concentration measurement in slurry systems ($\epsilon_s < 15$ vol. %). In the next section a novel technique for solids holdup determination will be discussed that may offer an alternative.

Experimental Setup and Procedure

Validation of the novel technique for solids holdup measurement was performed in a stirred cell. In this way suspension homogeneity could be ensured allowing calibration of the technique in a liquid-solid system. By letting gas bubbles of different sizes pass through the measurement volume, the situation encountered in slurry bubble columns was approximated. The main advantage of the approach followed is that it allows the technique's validation, since solids concentration is also known in the three-phase situation. Note that, within the framework of this article, solids concentration is based on liquid-solid slurry volume and can therefore be calculated from

$$\epsilon_S = \frac{M_S/\rho_S}{V_L + (M_S/\rho_S)} \tag{3}$$

A baffled flat-bottomed stirred cell (Figure 1A) made of glass and possessing a height of 96 mm and a diameter of 50 mm was applied in the experiments. The cell was equipped with a downwards pumping pitch bladed turbine stirrer (45° pitch angle, 4 blades of 6 mm). The stirrer possessed a diameter of 26 mm and was positioned in the center of the stirred cell at 9 mm from the bottom. The center of the constructed probe (Figure 1B) was placed 14 mm eccentrically, while its lowest point was positioned at 22 mm from the bottom. Temperature in the stirred cell was measured using a thermometer. Air was injected using a needle possessing a hole of 1 mm positioned 17 mm eccentrically at 25 mm from the bottom. The distance of the needle to the measurement volume of the probe was 10 mm in the majority of the measurements.

Glass beads ($\rho_s = 2.9 \times 10^3$ kg·m^{-3}) possessing a volume average diameter of 61 μm and a standard deviation of 5 μm were applied as the solid phase. They were coated by the Phosphors & Multiforms product unit of Philips Components in Eindhoven (The Netherlands) with 1 wt. % $Y_2O_2S{:}Eu^{3+}$, a red/orange light emitting phosphor. To create a fluorescent liquid phase, the sodium salt of fluorescein, a yellow/green light emitting phosphor, supplied by Aldrich was dissolved at a concentration of 4 mg/L. Since the fluorescence intensity

Table 1. Comparison of Techniques Considered for Determining Solids Holdup in Gas-Liquid-Solid Slurry Systems

Technique	Solids Holdup	Holdup Range	Phase Comb. Proven For*	Accuracy	Hydrody. Disturb.	Phase Alter.	Local Value	Remarks
Sampling	ϵ_S	< 0.10	G-L-S	+	–	None	±	Laborious
Electrical Conductivity	$\epsilon_S^{\#}$	0.02–0.50	G-L-S	+	–	None	–	Direct Measurement in Three-Phase Systems Impossible
Electromagnetic Permeability	$\epsilon_S^{\#}$	0.04–0.60	G-L/G-S	+	+	None	–	
Ultrasonic Sound Distortion	$\epsilon_S + \epsilon_S^{\#}$	≤ 0.05	G-L-S	–	+	None	–	
Ferromagnetic Tracer Particles	$\epsilon_S^{\#}$	< 0.20	G-L-S	?	+	S	–	
Reflection Fiber Probe	$\epsilon_S^{\#}$	0.30–0.45	G-L-S	+	–	None	+	
Fluoroptic Technique	ϵ_S	≤ 0.15**	G-L-S	+	–	L+S	+	Liquid-Solid Calibration Suffices

*Only most complex combinations mentioned.
**Outside this range applicability not proven, but likely.

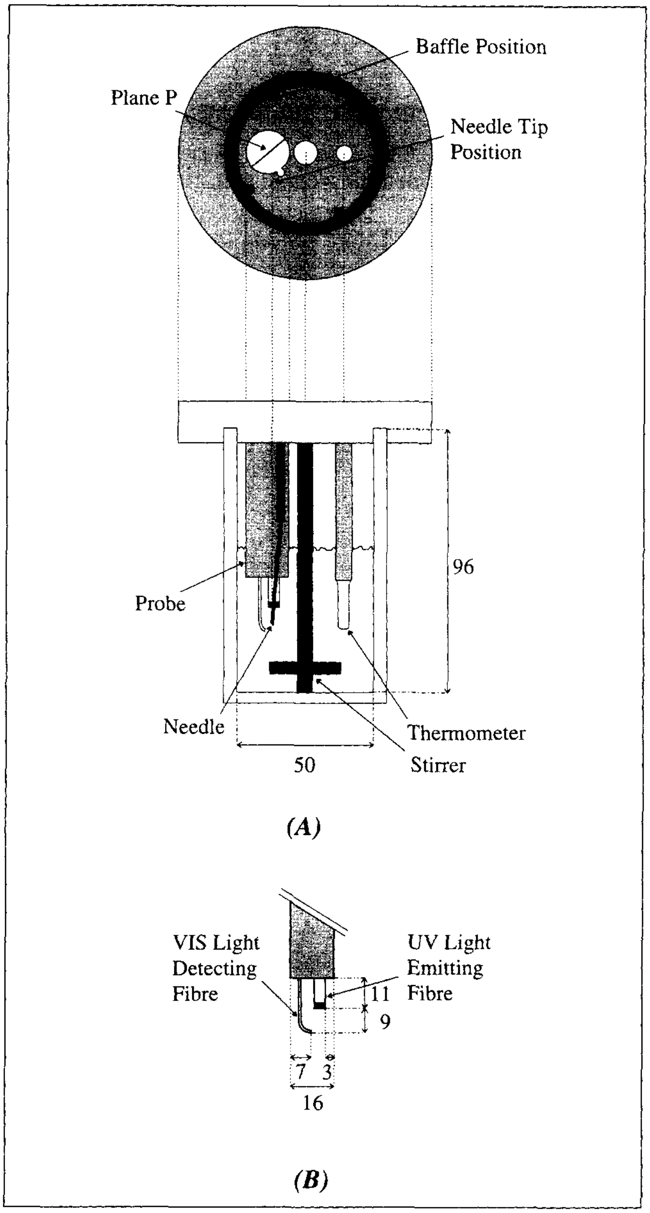


Figure 1. Experimental setup (dimensions in mm, drawn to scale).

(A) Top and front view of the stirred cell (P = vertical plane containing the heart lines of both fibers of the probe); (B) front view of the probe tip (normal to plane P).

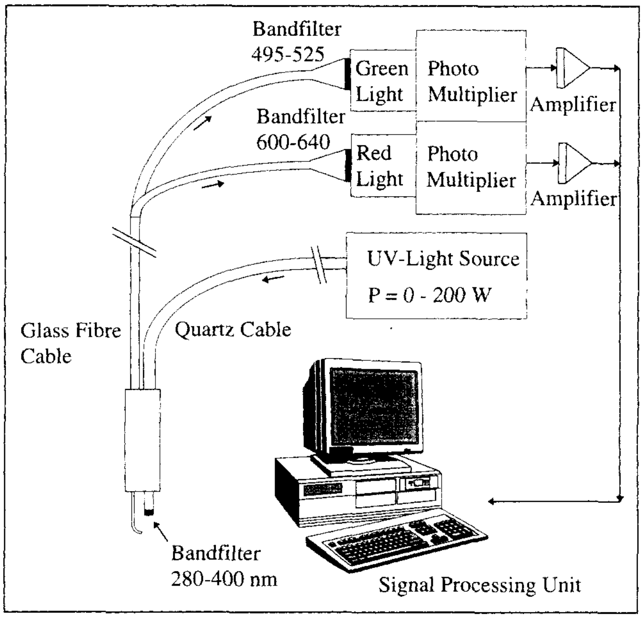


Figure 2. Measurement system.

of fluorescein strongly depends on pH below a value of 8, but remains constant at higher values of pH (Diehl, 1989), an aqueous solution buffered at pH = 9.0 was used. Air was the applied gas in the three-phase experiments. To prevent foaming of the three-phase system 0.1 vol. % Afranil obtained from BASF was added to the liquid phase.

In the experiments 100 mL of buffered fluorescein solution was present in the stirred cell. Temperature was controlled at 30°C by submerging part of the stirred cell in a thermostated vessel. Before adding particles to the system, they were cleaned with ethanol and subsequently dried. The weighed amount of particles present was gradually increased from 0 to 51 grams. Since adding solids to the stirred cell necessitated its temporary removal from the thermostated vessel, the system was left to stabilize for some time after every addition. In all experiments stirring frequency was set at 1,590 rpm to attain suspension homogeneity. If desired, gas was injected through the needle tip at flow rates of either 0.2, 3 or 6 mL/s using syringes.

A mercury arc lamp (type USHIO USH-205S) acted as a source of ultraviolet light. In most of the experiments, the electrical dissipation in the light bulb amounted to 100 W. The light produced was transported through a quartz cable and passed a Schott DUG 11 filter (280–400 nm) before entering the fluorescent measuring medium (Figure 2). Light produced therein was detected using a bent glass fiber of Dolan and Jenner (angle 90°). The glass fiber guided the light produced to microscope oculars to create parallel bundles. Then two bandfilters were used to separate the light emitted by the measuring medium into two colors. An Omega Optical 510DF23 filter was used to select a wavelength interval of 495–525 nm (green light transmission), while red light (600–640 nm) was selected using an Omega Optical 620DF35 filter. The intensities of both colors were converted to electrical signals using Hamamatsu R928 photomultipliers and amplification circuits. Further details of the electrical part of the detection system can be found in Wagenaar et al. (1995).

The electrical signals were read by an IBM-compatible computer. A Turbo Pascal program was used to collect data from the measurement system. In a single run lasting 5 s, 15,500 values were detected for the intensities of both visible colors. At the end of the run, measured data could be saved to file, while the average red signal, the average green signal, and their ratio were calculated and displayed on screen.

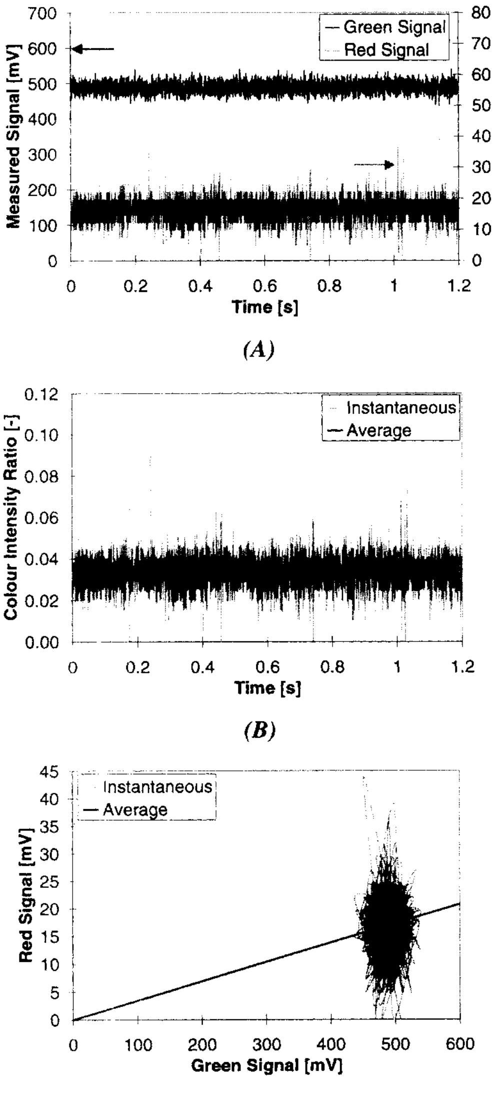
Results and Discussion

Preliminary experiments

Average signal intensities in the solids concentration range considered were found to be insensitive to stirring frequency if its value exceeded 1,500 rpm. Therefore, in all experiments, stirring frequency was set to 1,590 rpm to achieve homogeneous suspension of the particles. At a solids holdup of 5 vol. %, the incident UV intensity was varied over a broad range by gradually changing the power applied to the mercury arc lamp from 60 to 160 W. Even though the average signals of both colors varied by a factor 5, their ratio only changed by 7%. This ratio therefore seems to be a robust measure for solids concentration. Upon variation of temperature from 20 to 40°C, the ratio of the average color intensities increased by 15%, which could mainly be attributed to a decrease of the measured average green intensity.

Liquid-solid system

The influence of solids concentration on measured intensities and their ratio was investigated in the range of 0 to 15 vol. %. Instantaneous values were used to reconstruct the measured red and green signals as a function of time. Throughout this article, three different representations are used for this kind of data. The first (*A*) shows the time dependency of the two individual signals during a certain time interval, while the second (*B*) shows the behavior of their ratio, the color intensity ratio (CIR) in the same period. In the third representation (*C*) for the same time interval instantaneous red signals are plotted as a function of the corresponding green signals. The last representation, the contour plot, can be used to establish the extent of correlation between the two measured signals. As can be seen from Figures 3 and 4 both for a liquid and a liquid-solid system, noisy signals are measured for both color intensities and their ratio. Therefore, average values need to be used to characterize the system for a certain solids concentration. Applying a 25 s average for color intensity ratio, measured values could be



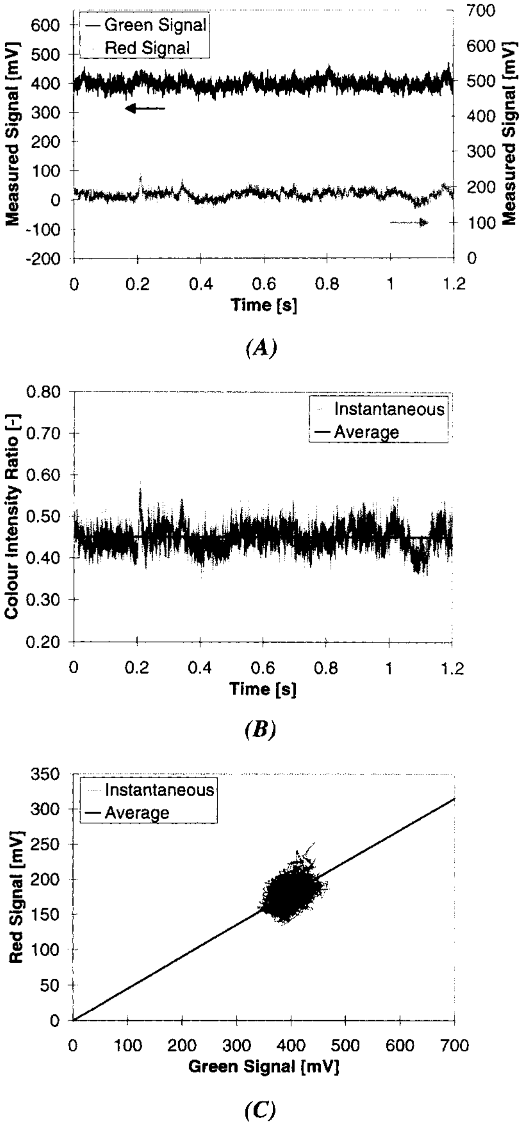
(*A*)

(*B*)

(*C*)

Figure 3. Response of liquid in the absence of solids (no gas flow).

(A) Time dependency of color intensities; (B) time dependency of color intensity ratio; (C) contour plot of measured color intensities.



(*A*)

(*B*)

(*C*)

Figure 4. Response of a 2 vol. % liquid-solid suspension (no gas flow).

(A) Time dependency of color intensities; (B) time dependency of color intensity ratio; (C) contour plot of measured color intensities.

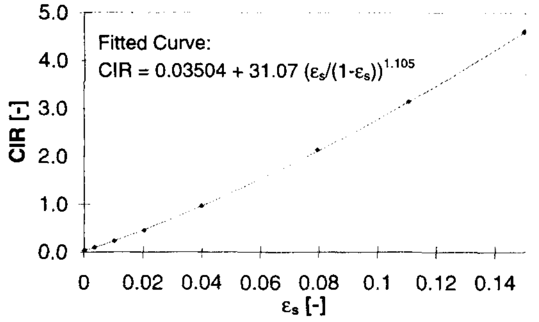


Figure 5. Two-phase calibration curve.

reproduced within 2%. A calibration curve for liquid solid systems then was constructed relating this average CIR to solids concentration (Figure 5). Measured data could be well described by the following equation

$$CIR = A + B\left(\frac{\epsilon_S}{1-\epsilon_S}\right)^C$$

$$A = 0.03504$$

$$B = 31.07$$

$$C = 1.105 \qquad (4)$$

The shape of the equation can be understood as follows: the irradiated liquid besides green light also produces a small amount of red light (Figure 3). On the other hand, irradiated particles only produce red light. If the amounts of light produced are assumed to be proportional to the volume fraction of the phase where they originate from, it follows

$$CIR = \frac{\phi_{R,S}\epsilon_S + \phi_{R,L}\epsilon_L}{\phi_{Gr,L}\epsilon_L} = \frac{\phi_{R,L}}{\phi_{Gr,L}} + \frac{\phi_{R,S}}{\phi_{Gr,L}}\left(\frac{\epsilon_S}{1-\epsilon_S}\right)$$

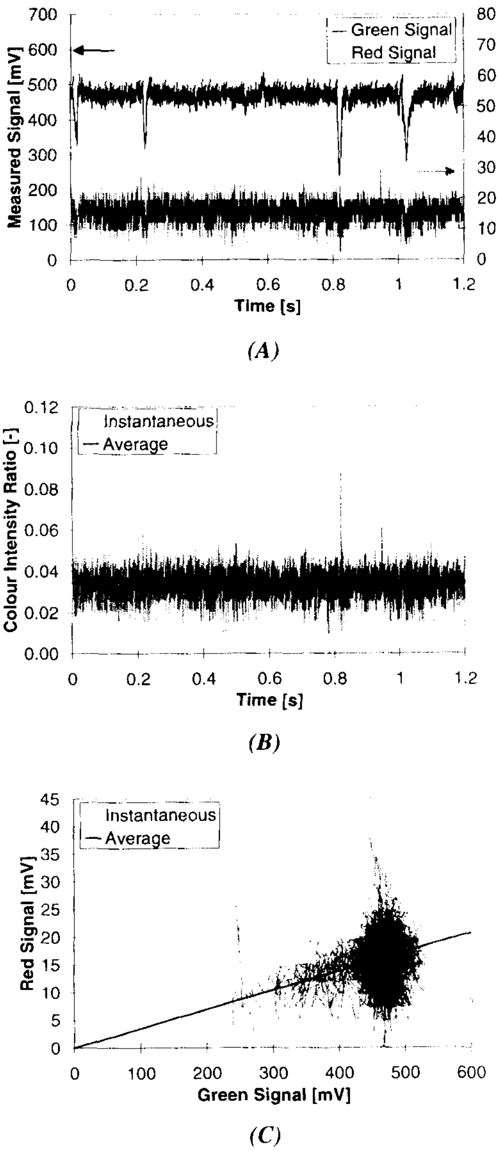
$$= A + B\left(\frac{\epsilon_S}{1-\epsilon_S}\right) \qquad (5)$$

The exponent C is added in Eq. 4 to increase flexibility of the fitting function. Its optimal value being close to 1 indicates the validity of the rather crude approach followed in deriving Eq. 5.

The stability of the phosphors and the measurement system was checked by performing a durability test for a number of days at a solids concentration of 2 vol. %. No decreasing trend was observed for the signal intensities, while the measured average ratio varied less than 1.5 percent.

Gas-liquid-solid system

In the absence of solids the position of the needle was varied until it was visually observed that formed bubbles passed through the measurement volume. Gas-flow rate was varied to allow for different bubble formation regimes. In Figure 6 signals are shown detected by the probe for a liquid system in which small bubbles (3–5 mm) rose through the measurement volume. These bubbles were formed at a gas-flow rate of 0.2 mL/s. Even though large broad spikes can be observed in the individual signals, their ratio is rather insensitive to bubble passage. This can also be seen when comparing the contour plots of the gassed (Figure 6C) and the ungassed system (Figure 3C). The signal characteristic to the ungassed system can also be found in the plot for the gassed system. In addition the latter contains a tail of data points which surrounds the average ratio line at low intensities, indicating that the signals remain correlated.



(A)

(B)

(C)

Figure 6. Response of liquid in the absence of solids (gas flow = 0.2 mL/s).

(A) Time dependency of color intensities; (B) time dependency of color intensity ratio; (C) contour plot of measured color intensities.

At a gas-flow rate of 6 mL/s, a jet of large bubbles (6–10 mm) was observed to pass through the measurement volume. The response of the signals measured for a slurry containing 2 vol. % of solids to a step in gas-flow rate is depicted in Figure 7. The individual signals show huge spikes and a large decrease of average signals, whereas their ratio shows moderate spikes at a slightly elevated average ratio. Comparing the contour plots (Figures 4C and 7C) of the gassed and the un-

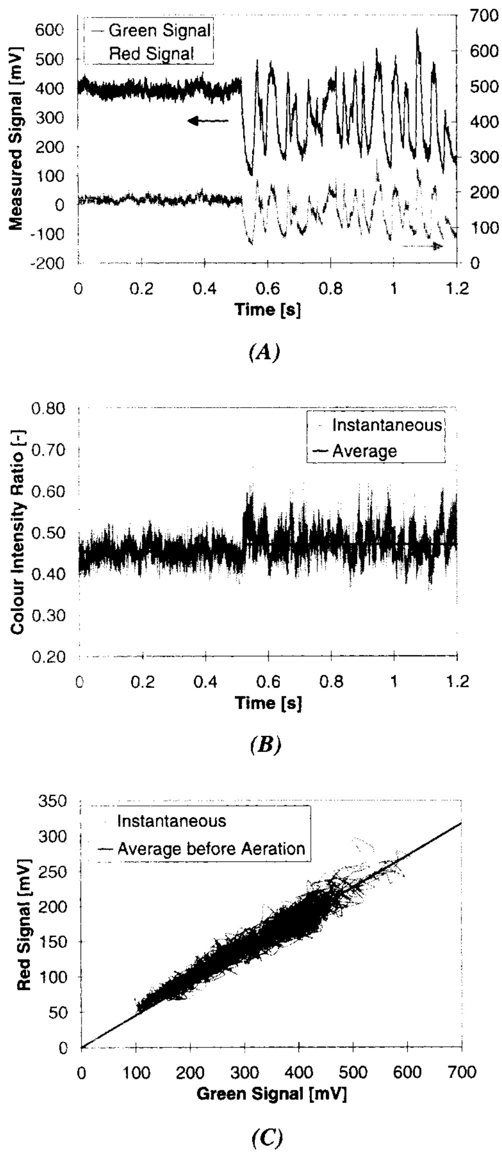


Figure 7. Step response of a 2 vol. % liquid-solid suspension (gas flow = 6 mL/s).

(A) Time dependency of color intensities; (B) time dependency of color intensity ratio; (C) contour plot of measured color intensities.

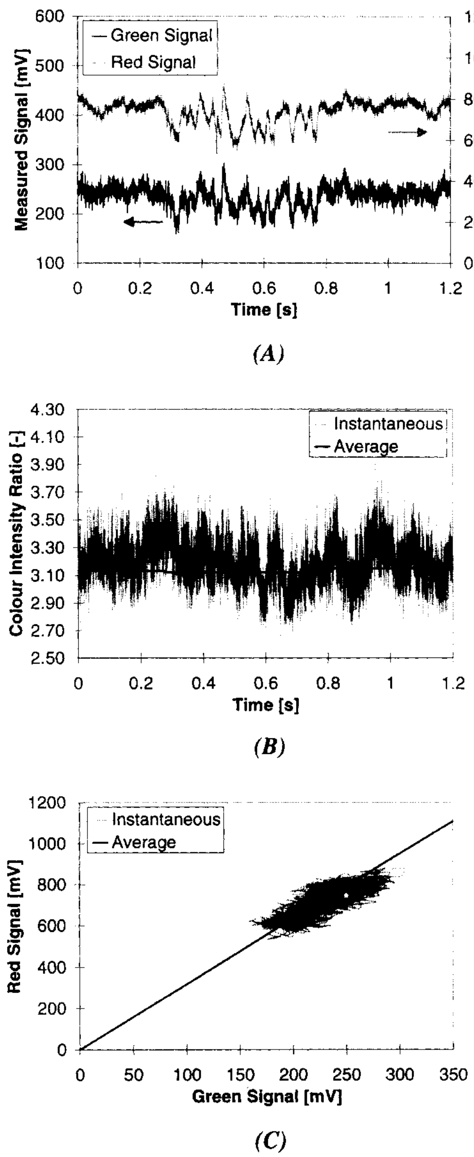


Figure 8. Pulse response of an 8 vol. % liquid-solid suspension (gas flow = 3 mL/s).

(A) Time dependency of color intensities; (B) time dependency of color intensity ratio; (C) contour plot of measured color intensities.

gassed system, it is again found that gas disturbance leads to curve broadening along the average ratio line. Only at low signal intensities, measured data slightly deviate from the average ratio line.

The signals measured for a slurry containing 8 vol. % of solids subjected to a pulse in gas flow rate (3 mL/s) show a slight decrease in average ratio due to gas flow (Figure 8). Again, the individual signals show much stronger variations than their ratio. Note that the three averages depicted are taken over short time intervals and do therefore include system oscillations. Therefore, it is not surprising that the average ratio does not return to its initial value after the pulse.

The three types of three-phase experiment discussed were performed with similar results over the full concentration range considered. Small bubbles (3–5 mm) passing sequentially did not influence the average CIR, while jets of larger bubbles (6–10 mm) only slightly influenced it. The largest deviations from two-phase measurements were observed for responses to a step in gas-flow rate (6 mL/s). From averages of measured CIR values corresponding to the aerated part of these responses, solids holdups can be calculated using the two-phase calibration curve, while the actual solids holdup follows from Eq. 3. Deviations between calculated and actual values amounted to less than 5% over the full concentration range considered (Figure 9). Data obtained for two different positions of the gas injection needle at 2 vol. % of solids also showed this behavior. It can be concluded that the relative measurement error for three-phase systems is less than 5%. Thus, the accuracy of the novel technique is high as compared to other techniques (such as ultrasonic sound wave dis-

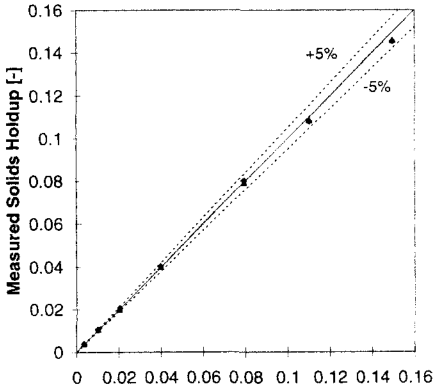


Figure 9. Parity plot of three phase measurements.

tortion). Further note that calibration of the fluoroptic technique only requires measurements in a liquid-solid system, while it is also applicable to a three-phase system. The technique does, however, require alteration of both the liquid- and the solid-phase properties, which cannot always be realized in practice.

Broadness of applicability

The technique developed is not limited to the present combination of phosphors or to aqueous media. Fluorescent dyes are available for aqueous, as well as organic systems. Different phosphors may be added to the solid phase even in a different way (see, for example, Wagenaar et al., 1995). The above results imply that any phosphor combination may work as long as the following criteria are met:

- No or only a small overlap should exist between the ranges of wavelengths at which both phosphors emit visual light.
- Visual light emitted by one phosphor should not be able to excite the other.
- The phosphor added to the solid phase should not erode from the particle or dissolve in the liquid.

Conclusions

A novel fluoroptic technique has been developed for measuring solids holdup in multiphase systems. For a liquid-solid system, a relative accuracy of 2% was obtained over the full concentration rate considered (0–15 vol. %). For a three-phase system, the maximum relative measurement error only increased to 5%.

Our fluoroptic technique possesses a very high accuracy as compared to other measurement techniques. A weak point of the present technique, however, is the necessity to alter both fluid phases, a requirement which cannot always be met in practice.

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Notation

g = gravitational force per unit mass, $m \cdot s^{-2}$
M = mass of a certain phase present in the stirred cell, kg
p = (static) pressure, $kg \cdot m^{-1} \cdot s^{-2}$
V = volume of a certain phase present in the stirred cell, m^3
z = axial coordinate, m
ϵ = phase holdup based on liquid/solid slurry volume
= phase volume/(liquid volume + solid volume)
$\epsilon^{\#}$ = phase holdup based on gas/liquid/solid slurry volume
= phase volume/(gas volume + liquid volume + solid volume)
ρ = density, $kg \cdot m^{-3}$
φ = specific light production rate, $V \cdot m^{-3}$

Subscripts

G = gas phase
Gr = green (light)
L = liquid phase
R = red (light)
S = solid phase

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