

A Compact Photon-Correlation Spectrometer for Research and Education

**I. K. Yudin,¹ G. L. Nikolaenko,¹ V. I. Kosov,¹ V. A. Agayan,²
M. A. Anisimov,^{2,4} and J. V. Sengers^{2,3}**

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A compact photon-correlation spectrometer for basic and applied research in physics, chemistry, biology, medicine, engineering, and environmental technology as well as for educational laboratory courses in these subjects has been developed. The instrumental setup enables one to make absolute measurements of the sizes of particles suspended in liquids in the range from 0.001 to 5 μm . The measurements are fast, lasting usually from seconds to several minutes. Real-time size monitoring, such as of kinetic aggregation processes, is also possible. The optical arrangement of the spectrometer even makes it possible to measure light scattering in opaque systems which are characterized by strong light absorption. The quantity of the sample to be studied can be quite small, starting from 0.01 cm^3 . The system includes specially designed software for performing data interpretation and for implementing fitting procedures, for exchange of data with other programs, and for automation of measurements of long duration or of sequences of measurements. Measurements verifying the accuracy of the system are presented for latex suspensions, for aniline dye dissolved in water, and for dilute solutions of polystyrene in toluene.

KEY WORDS: diffusion; light scattering; liquid mixtures; particle sizes; photon-correlation spectroscopy; viscosity.

¹ Laboratory for Phase Transitions and Critical Phenomena, Oil & Gas Research Institute of the Russian Academy of Sciences, 117917 Moscow, Russia.

² Institute for Physical Science and Technology, University of Maryland, College Park, Maryland 20742, U.S.A.

³ Department of Chemical Engineering, University of Maryland, College Park, Maryland 20742, U.S.A.

⁴ To whom correspondence should be addressed.

1. INTRODUCTION

In various scientific and engineering tasks there is a need to investigate and characterize dispersed systems. Specifically, in fluid dispersions, solid, liquid, or gas particles are suspended in a fluid medium. A knowledge of the sizes of such particles in suspensions and/or of the viscosity of the fluid is important for developing and controlling many chemical engineering processes. There exist many particle-sizing methods, partly because none of them covers all sizes of interest [1]. For sizes in the range from 0.001 to 5 μm , photon-correlation spectroscopy (PCS) is the most suitable and advanced technique. Several books deal with the theory and practice of PCS and related methods [2–7]. The ideas of optical-mixing spectroscopy and optical heterodyning that are the genesis of the PCS were pioneered by the Russian theoretician Gorelik [8]. The first experimental realization of these ideas was performed by American scientists [9]. The main problem delaying the practical application of PCS was the absence of an appropriate light source with narrow linewidth (monochromatic) and high intensity. This problem was solved in 1961, when a gas laser was invented and Forrester started to use the laser for optical-mixing spectroscopy [10]. Pecora [11] showed that temporal fluctuations of scattered light contain information concerning the motion of the particles. This idea connected the light-scattering method with modern problems in condensed-matter physics, colloidal chemistry, and biology. The first application of optical-mixing spectroscopy as a new experimental method for measuring the diffusion coefficient of dilute polymer solutions was reported by Cummins et al. [12]. The first studies of the thermal diffusivity of a fluid near the critical point by optical spectroscopy was reported by Ford and Benedek [13] and by Alpert [14]. The next technical challenge was posed by the low efficiency of signal analyzers for weak light-scattering signals. This difficulty was overcome in the 1960s during the microelectronics revolution when a new analyzing device, namely, a real-time digital correlator, was developed. Ford et al. [15] developed the first light-scattering setup including a digital real-time correlator. This form of PCS exists to the present time. A significant new step forward was the single-board digital correlator to be used in personal computers [16]. In addition, novel photon detectors and laser diodes were developed. All these inventions have led to simple low-cost PCS systems for a wide range of applications. Some of these applications are listed in Table I.

The photon-correlation spectrometer *PHOTOCOR Complex* presented here is based on the PCS technique and designed for measuring submicron particle sizes, diffusion coefficients, viscosities, and molecular weights of polymers; it can be used for both basic and applied research. It does not

Table I. Fields of Application of the PCS Method

Physics and chemistry	Colloidal and polymer dispersions, micelles, microemulsions, vesicles, latexes, gels, soles, liquid crystals, nucleation and aggregation processes, chemical reaction kinetics, phase transitions, and critical phenomena
Biology and medicine	Cells, viruses, proteins, membranes
Chemical engineering	Pigments, dyes, glues, powders, lubricants, petroleum and fuels, mud, membrane filters, and ultrafiltration testing
Environmental technology and food processing	Disperse pollution, food quality testing
Education	Novel labs for physical, chemical, biological, and engineering education

require specially trained personnel or sophisticated or expensive maintenance. The apparatus has been developed by the Photon Correlation Group of the Oil & Gas Research Institute of the Russian Academy of Sciences. Most recently, one of the systems has been installed at the Undergraduate Chemical Engineering Laboratory at the University of Maryland, to offer Chemical Engineering students a laboratory course which includes the PCS technique and its applications.

2. PHOTON-CORRELATION SPECTROSCOPY

The PCS method is used to determine the velocity distribution of particles in suspension by measuring the dynamic fluctuations of the intensity of scattered light [3, 4]. The disperse particles or macromolecules suspended in a liquid undergo Brownian motion. This motion causes fluctuations of the local concentration of the particles resulting in local inhomogeneities of the refractive index. This in turn leads to Rayleigh scattering spectrum with linewidth Γ (defined as the half-width at half-maximum), which is proportional to the diffusion coefficient D of the particles [3]:

$$\Gamma = Dk^2 \quad (1)$$

where $k = (4\pi n/\lambda) \sin(\Theta/2)$, n is the refractive index, λ the laser wavelength, and Θ the scattering angle. Assuming the particles to be spherical and non-interacting, one can obtain the mean radius r from the Stokes-Einstein equation

$$r = k_B T / 6\pi\eta D \quad (2)$$

where k_B is Boltzmann's constant, T the temperature, and η the shear viscosity of the solvent.

The desired information can be obtained from the autocorrelation function of the scattered-light intensity, which, for the simplest case of spherical monodisperse noninteracting particles in a dust-free fluid, has a characteristic decay time τ_c which is the inverse of the linewidth Γ . Therefore, the diffusion coefficient and either the particle size or the viscosity can be found by fitting the measured correlation function to a single-exponential decay.

Two techniques exist for measuring the correlation function: heterodyning and homodyning. In heterodyne measurements, which are most suitable for small intensities, the scattered light is mixed coherently with a static light source at the incident wavelength and the static field is added to the scattered fields at the photodetector. Equation (1), relating the linewidth Γ to the diffusion coefficient D , is applicable for heterodyne experiments. In homodyne measurements the photodetector receives scattered light only. Homodyning is most suitable for large intensities (e.g., near the critical point of a fluid or for colloid systems). For the homodyne spectrum the relation between Γ and D reads [3]

$$\Gamma = 2Dk^2 \quad (3)$$

The *PHOTOCOR Complex* system can operate in both the homodyning and the heterodyning mode. The results presented in this paper were obtained with homodyne measurements.

The autocorrelation function $G(\tau)$ of the scattered light as a function of the delay time τ can be represented by

$$G(\tau) = b[1 + \varepsilon \exp(-\tau/\tau_c)] \quad (4)$$

where the baseline (accidental) correlation level b is proportional to the total intensity I . Such a correlation function is shown schematically in Fig. 1. The coefficient ε depends on the amount of stray light and the apertures in the system, but ε is always less than unity. The size r calculated from Eq. (2) is referred to as the hydrodynamic radius. It may be larger

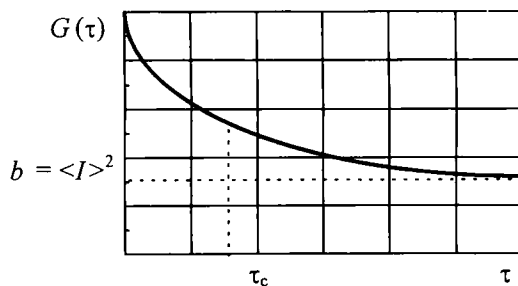


Fig. 1. Schematic autocorrelation function of the intensity of scattered light.

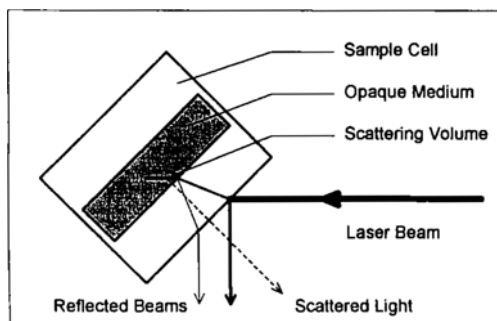


Fig. 2. Optical scheme for measuring light scattering in opaque liquids.

than the actual radius of the bare particles because of the presence of possible layers of solvent, surfactant molecules, or (for charged particles) associated ions. In most cases these layers add a negligible amount to the size except for the smallest measurable sizes.

We have also developed an original technique to study nontransparent disperse systems, when the opacity makes measurements of particle sizes by light scattering very difficult [17]. The problem involves two related challenges: strong light absorption in the sample hampering detection of the scattered light and a complex refractive index creating difficulties for the correct interpretation of the data [18]. A modified optical scheme to perform particle-size measurements in opaque liquids is shown in Fig. 2. A rectangular sample cell is placed at an angle of 45° with respect to the incident laser beam. The optical axis of the photodetecting system is normal to the front plane of the sample cell. The scattered light is collected from the region where the laser beam enters the sample. A special asymmetric holder allows one to change the position of the scattering volume to study light scattering in the corner or near the wall of the cell, as well as in the bulk of the fluid. The laser beam is attenuated by a neutral glass filter to avoid thermal-lens effects. The conventional 90° geometry with the scattering volume placed at the corner of the sample cell can also be used for some very dilute but still opaque solutions. A number of test measurements with some model opaque liquid systems have verified the adequacy of this experimental approach [17, 19].

3. CHARACTERISTICS OF EXPERIMENTAL SYSTEM

3.1. Principal Scheme

The principal arrangement of the system is shown in Fig. 3. It has features that are typical for multipurpose installations for studying both

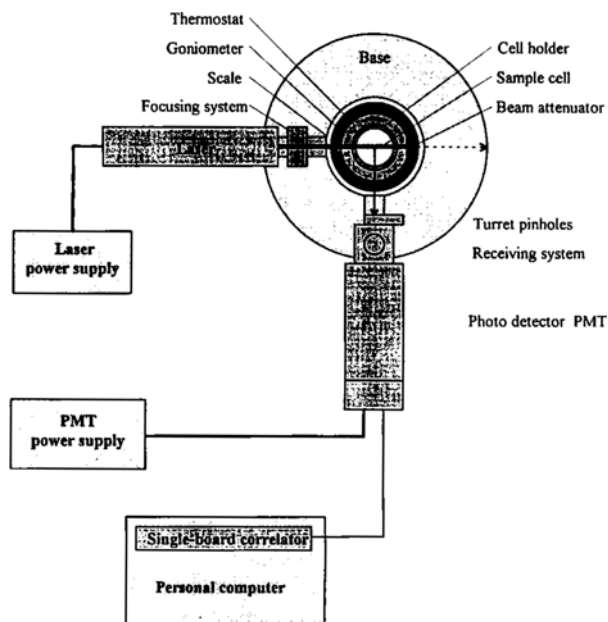


Fig. 3. Principal schematic of the *PHOTOCOR* Complex correlator system.

static (intensity) and dynamic (time-dependent correlation function) light scattering. The optical bench and precision goniometer are based on a massive disk-shaped base. A *He-Ne* laser and the focusing system are fixed on the bench. The receiving system (photodetecting unit) is located on a rotating goniometer arm. The thermostat and the cell holder are coaxial with the goniometer axis. The output signal produced by the photodetecting unit is analyzed by a single-board multichannel correlator which is plugged into a personal computer. The personal computer performs the data analysis and instrument control. The photo-detecting system consists of an efficient receiving optical system with turret with six pinholes for selection of aperture, a low-noise photomultiplier tube (PMT) operating as a photon-counting system, and an amplifier-discriminator. The *PHOTOCOR* PMT Power Supply unit is housed in a metal-grounded enclosure suitable for mounting on an optical table.

3.2. Performance and Physical Specifications

The range of particle sizes that can be measured extends from 1 to 5000 nm, with diffusion coefficients between 10^{-13} and $10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$. The

precision goniometer allows one to study light scattering at scattering angles varying from 0 to 140° with a goniometer resolution of 0.1°. The minimum collection aperture angle is 0.11°. The sample cell is located inside a thermostat which is connected to a water bath capable of maintaining a constant temperature between 0 and 100°C with a precision of 0.1°C. The thermostat is supplied with holders for various sample cells: standard precision optical-glass or silica square cells 12.5 × 12.5 mm, produced by Hellma Cells, Inc.; plastic square cells 12 × 12 mm; round glass cells with diameters of 14.75, 16.25, 27.25, and 30 mm; and an asymmetric holder for studying opaque systems. A simple low-intensity *He-Ne* laser is used (05-LHP-121, Melles Griot) or a more powerful *He-Ne* or ion laser. Selected PMT's for photon counting are used (FEU-79 or PEU-136, Russian-made) with the following characteristics: 14 dynodes, 1.7 to 1.9 kV, dark count rate 20 to 50 pulses/s, pulse width of 15 ns, quantum efficiency at 633 nm of 4 to 6%, and maximum efficiency of 20% at 400 nm.

3.3. Correlator

The installation includes an original single-board multichannel 16-bit correlator *PHOTOCOR-SP* as a full AT-compatible bus card to be plugged into an EISE bus slot in a 486 or Pentium-class IBM PC or a compatible PC running Microsoft Windows or Windows'95 operating system. A new approach has been used for the design of this device: a universal analyzing hardware board and a specific control software have been developed. The hardware board is based on the digital signal processor TMS320C26. Another single-board correlator *PHOTOCOR-M* which contains specially designed state-of-the-art integrated circuits has also been developed. The correlators provide both linear and nonlinear time-scale channel spacing. In the linear mode all points of the measured correlation function are spaced equidistantly in time. This is optimal for measuring single-exponential correlation functions (monomodal particle-size distributions) as well as periodical correlation functions (velocity measurements). The nonlinear quasi-logarithmic channel spacing is very efficient for measuring multi-exponential correlation functions (polymodal or wide-particle size distribution). Correlator channels are sectioned into four blocks, the channels within each block being spaced linearly in time. The sample times are different for each block: T_{S1} , $T_{S2} = n_1 T_{S1}$, $T_{S3} = n_2 T_{S2}$, and $T_{S4} = n_3 T_{S3}$, where the factor n_i is 2 for the *PHOTOCOR-SP* and can be tuned from 1 to 16 for the *PHOTOCOR-M* correlators. Two nonlinear modes are available, namely, multiple-tau and variable-time expansion (*VTE*). In the multiple-tau mode, four blocks of channels are arranged

Table II. Features of the *PHOTOCOR-SP* and *PHOTOCOR-M* Correlator Boards

Specification	<i>PHOTOCOR-SP</i>	<i>PHOTOCOR-M</i>
Processing (delayed signal \times instantaneous signal)	16 \times 16 bits	8 \times <i>N</i> bits
Clock time	40 MHz	40 MHz
Capacity of each channel	48 bits	39 bits
Minimum sample time	100 ns	100 ns
Minimum sample time in real-time mode	17 μ s	100 ns
Maximum sample time	1 s	0.15 s
Number of channels (linear mode)	64 ... 255, autoadjustable	72
Number of channels (multiple-tau mode)	30 + 15 + 15 + 15, factor 2	16 + 16 + 16 + 24, factor 2 ... 16
Number of channels (VTE mode)	—	16 + 16 + 16 + 24, factor 2 ... 16
Baseline delay, in sample-time units	—	Up to 4096
Number of monitor channels	—	7
Dimensions	235 \times 120 mm	340 \times 115 mm
Power requirements	5 V \times 0.6 A	5 V \times 1.2 A
Operation modes	Auto- and cross-correlation	

sequentially on the time axis: the last channel of the previous block is the first channel of the next one. In the *VTE* mode, the four blocks of the correlator operate independently as separate correlators with the time scale for each block beginning at zero. The choice of mode is dictated by experimental conditions. The features of the correlators are summarized in Table II.

A special fast algorithm has been developed for processing the correlation functions with the TMS320C26. A number of other algorithms are available, to transform the hardware board to the spectrum analyzer, probability distribution analyzer, multichannel counter, etc.

The *PHOTOCOR-SP* and *PHOTOCOR-M* correlators can be used simultaneously with the same computer, for example, when studying systems containing particles of two appreciably different sizes. The signal from the photodetector is divided and supplied to the inputs of both correlators. The sample times for the correlators are different (to cover a selected range of particle sizes) and are chosen in such a way that each correlator operates in a real-time mode. Using both correlators, one obtains a powerful analyzing device that combines the advantages of each board.

We have developed a set of programs (*PHOTOCOR Soft*) to control and plan measurement processes and to perform data fitting and analysis. The main window of the program is shown in Fig. 4 with the four open windows: the *Display* window to monitor the accumulation of the correlation function, signal intensity changes, and other signal properties; the *Control* window to set constants and some correlator intrinsic parameters; and the *Points* and *Cumulants* windows to process accumulated data and display fitting results. To simplify measurement control and data analysis, the program has its own built-in command interpreter to create and use various sets of commands that together accomplish an assigned task. The interpreter includes all possible commands that may be accessed via the program menu or dialogue boxes (e.g., correlator control, setting constants, etc.)

An extremely important feature of the correlator board is that it accumulates data by itself, after all necessary initializations have been performed, without interfering with most program operations, so that *PHOTOCOR Soft* may be exited or be used to process previously saved data files. A dynamic linking from the correlator data to other Windows applications is provided, so that the system can be used fruitfully as part of a larger arrangement. A user can install his or her own routines for interpreting raw data directly to the program.

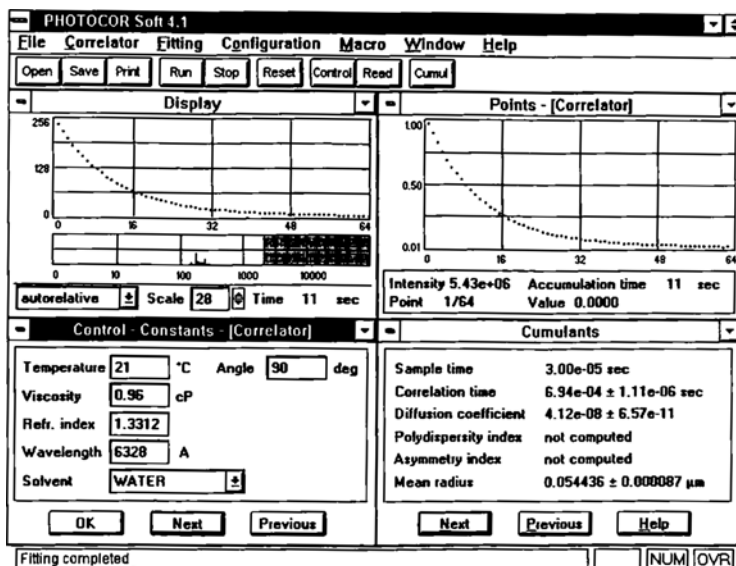


Fig. 4. Main window of the *PHOTOCOR Soft* software user screen.

4. EXPERIMENTAL TESTS OF THE INSTRUMENT

A number of experiments have been carried out to test the accuracy and resolution of the instrument.

(1) Calibration latexes with mean radii of 0.05, 0.1, 0.135, and $0.25\mu\text{m}$ were dispersed in deionized water. Each was specified to have a polydispersity distribution with width less than 6%. The latexes were produced and calibrated by the Lebedev Rubber Research Institute, St. Petersburg, Russia. These samples were measured and the errors of the determinations of the mean radius did not exceed 1.5% in each case, under the assumption that the polydispersity distribution is symmetrical.

(2) Particle-size measurements in an opaque system (black aniline dye dissolved in water) were also performed. The dye concentration was changed from that corresponding to absolutely transparent to opaque solutions. In the latter case the light penetration into the sample did not exceed 0.5 mm. As shown in Fig. 5, the measured radius is the same within $\pm 5\%$ for of all dye concentrations. The measurements were carried out with a 135° "backscattering" geometry. The conventional 90° geometry in a cylindrical cell has also been used at the one concentration corresponding to 0.01% (almost transparent) solution.

(3) In addition, we investigated weakly scattering systems, containing particles of much smaller radius, namely, dilute polymer solutions. Zhang et al. [20, 21] have recently determined the diffusion coefficient of dilute polystyrene solutions in toluene at 25°C with an optical beam-deflection technique [22].

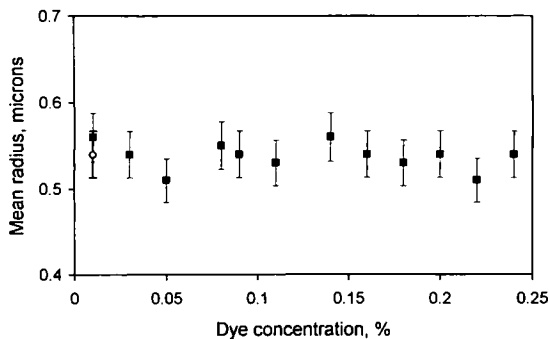


Fig. 5. Mean radius of black aniline dye particles dissolved in water for a number of dye concentrations: (○) 90° conventional geometry; (■) 135° "backscattering" geometry.

We measured the diffusion coefficient and the particle size of polystyrene of molecular weight $M_w = 96,400$ dissolved in toluene at 22°C using the *PHOTOCOR Complex* system. The mass concentration of the polystyrene was $0.0217 \text{ g} \cdot \text{cm}^{-3}$. Two optical geometries and sample cells were used: with scattering angles of 45° (a round glass cell with a diameter of 27.25 mm) and 90° (a square cell of 12.5×12.5 mm). The scattering in this system is very weak, so that the chosen sample times of 8×10^{-6} s (for 45°) and 3×10^{-6} s (for 90°) did not correspond to the real-time operation mode (which starts from 17×10^{-6} s for the *PHOTOCOR-SP* correlator); the correlator internal accumulation times used for the calculations (18 min for 45° and 40 min for 90°) were 5 to 12 times less than the actual clock time (240 min). Such sample time conditions are not favorable for accurate measurements. Nevertheless, we were able to obtain excellent agreement with the measurements of the diffusion coefficient of Zhang et al.

The values of the measured diffusion coefficient and of the effective radius obtained by various experimental techniques are presented in Table III. The errors in the last two columns in Table III represent standard deviations from fitting the correlation function to an exponential one. The errors in the determination of the scattering angle, temperature, concentration, etc., have not been accounted for explicitly, but we estimate them to be of the same order of magnitude as the fitting errors. Though the temperature of the measurements was 3°C higher than that of the measurements of Zhang et al., the corresponding change in the diffusion coefficient is not significant and the results agree within the accuracy of the measurements. The results obtained thus demonstrate the reliability and inherent accuracy of our instrument for determining diffusion coefficients and particle sizes.

Table III. Diffusion Coefficients and Particle Sizes of a Polystyrene-Toluene Solution Measured with Different Experimental Techniques^a

Experimental technique	Small-angle light scattering [20, 21]	Optical beam deflection [20, 21]	PHOTOCOR large-angle light scattering	
			45°	90°
Diffusion coefficient ($10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}$)	7.0 ± 0.2	6.9 ± 0.2	7.0 ± 0.2	7.0 ± 0.2
Effective radius according to Eq. (2) (nm)	5.4 ± 0.2	5.4 ± 0.1	5.4 ± 0.2	5.5 ± 0.2

^a Polystyrene concentration, $0.0217 \text{ g} \cdot \text{cm}^{-3}$.

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