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Automatized Photogoniodiffusometer and Coupling with Automatized Viscosimeter

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SUMMARY

We describe an automatized light scattering apparatus and its coupling with automatic viscosimeter and give some applications.

The laser technique development motivated several workers to construct various kinds of light scattering apparatus (1,2). Nevertheless, at our knwledge, a entirely automatized device with automatic dilution which avoids many fastidious handling has never been proposed. Moreover, the usual characterization of a polymer sample often requires, not only his molecular weight M_w and radius of gyration RG but also its intrinsic viscosity $[\eta]$. One of us (3) has, some years ago, constructed an automatic viscosimeter. Thus, it was natural to associate, in a same apparatus, the two types of technique, in order to determine, in a same experiment requiring only the preparation of one solution, the principal molecular parameters characterizing a polymer sample and its interaction with a given solvent.

A. INSTRUMENTATION

The block diagram of the instrument is represented in fig. 1.

1. Light scattering part

- apparatus description

The light scattering apparatus has been constructed according to the Wippler-Scheibling principle. The details of its construction are shown on Fig. 2 and they correspond to our aim to reduce the apparatus dimensions and to keep motionless the measurement cell, in order to avoid the variations of the multiple reflexions of the incident laser beam.

The system is contained in a tank (A) filled with xylene, surrounded by a water jacket (B) for thermostatation and the inner wall is blackened to reduce the reflexion effects. The cell rest (R) is fixed on the tank cover (K). The laser tube (U) (SORO 2mW - λ = 6320 Å) is supported by a ring (C) on the tank wall ; its good horizontality and direction can be obtained with 3 ajusting screws (D). The principal laser beam is selected by a simple diaphragm (E) set up behind the window (F). The scattered

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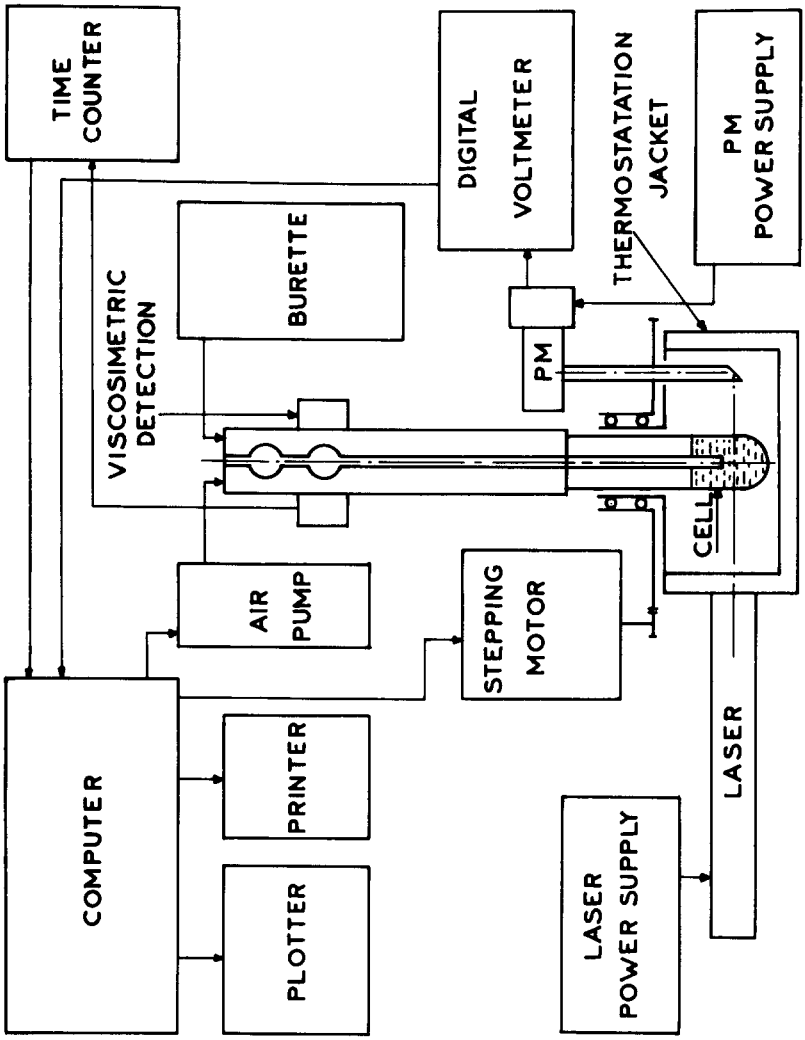

Figure 1 : Block diagram

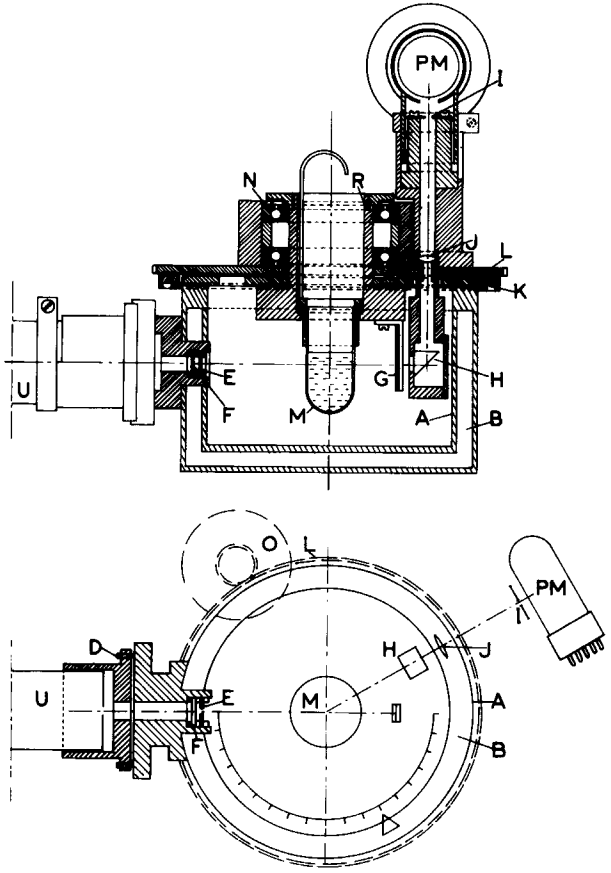

Figure 2 : Light scattering apparatus

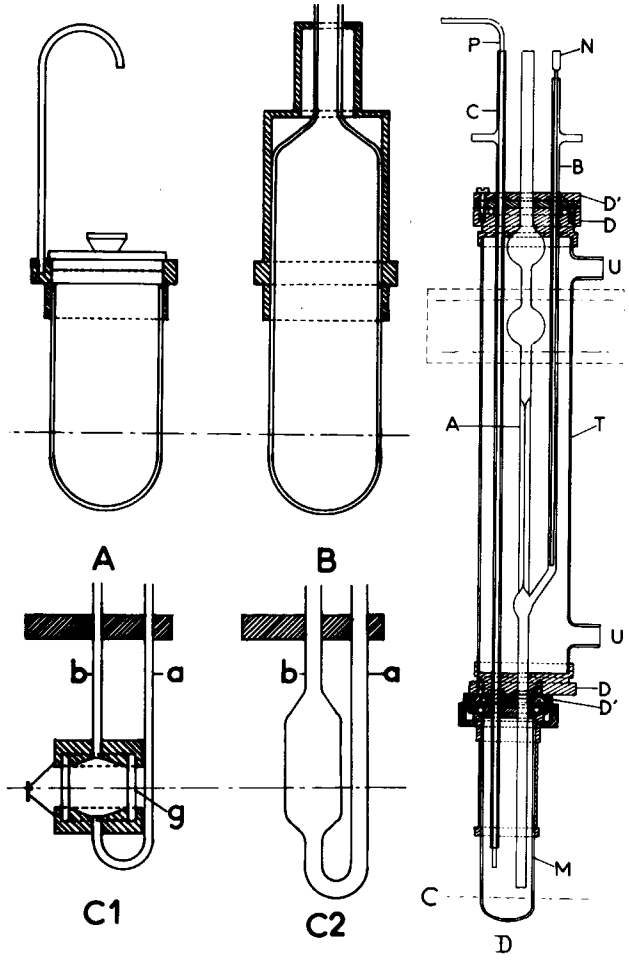

Figure 3 : Different cells

beam is collected by a prism (H) and reflected at right angle ; a lens (J) is used to give a picture of the scattering volume of the cell on a slit (I), set before the photomultiplier (PM). The prism and PM holder is fixed on a cogged and graduated cover (L) turning around the cell (M) axis, owing to a balls bearing (N) and drived by a stepping motor (O). Behind the cell, on the transmitted beam axis, is set a light trap (G) of black glass.

- Cells description

The apparatus is conceived to be used with anykind of cells which are represented in fig. 3.

i) classical glass cells of diameter ranging between 1 and 2.5 cm with contents of 2 until 10 cm^3 (A)

ii) the glass dilution cell (B) of 25cm diameter, 50cm^3 of total volume. Its upper part is contained in a metallic cylinder as holder. The liquid from the burette is introduced by a teflon tube

iii) Some cells for continuous flow which are usefull in applications such as the determination of M_w and R_G in the course of GPC experiment or during chemical cinetics. In this case, it is necessary to reduce the dimensions. The first cell, (C_1 fig. 3) is constructed from teflon pieces (T) and little glass cylinder (G), the tubings (a and b) being in stainless steel and its content is 1cm^3. The second one is entirely realized in glass, its volume being 2cm^3. In the two cases, the liquid is introduced by the lower tube (a), rises into the cell and goes out by the upper tube (b) to obtain a good circulation. An example of application of this type of cell is published elsewhere (6).

- Calibration

It was important to be sure of the rigourous verticality of the polarization plane of the incident beam ; for this purpose we have operated by successive approximations : a polarizer, set in the beam axis, is turned around its vertical geometrical axis, and the total light extinction is only obtained when the two planes of polarization of the incident beam and polarizer are simultaneously verticals. In these conditions, the quantity $I_\theta \sin / I_{\theta=90°}$, where θ is the scattering angle and I_θ the scattered intensity, must be equal to 1, whatever θ is . For a reference benzene, we have obtained the expected variation (5).

We used the constant K_V :

$$K_V = \frac{n_x^2}{R_{BV}} \frac{4\pi^2}{N_A \lambda_0^4}$$

where λ_0 is the wave-length, N_A the Avogadro number, n_x is the benzene refractive index and R_{BV} the benzene Rayleigh ratio since this substance is generally used for calibration.

By using the R_{BV} value, 11,84 10^{-6} cm^{-1} measured by Pike et al. (4), we can calculate K_V=0.779, which is in good agreement with the value 0.790, we have obtained with monodisperse polystyrene samples, the molecular weight of which being well known.

2. Viscosimeter-light scattering apparatus coupling

The combinated device is represented in fig.3D. We have used a tube of thick glass (T) which contains the Ubbelohde viscosimeter (A). Two lateral outlets (U and U') allow the thermostating water circulation. It is closed at its extremities by two metallic disks (D) through which pass the different tubes. The water tightness is obtained by rubber gaskets compressed by an other disk (D'). The lower disk holds the disconnectable fixation of the eccentred scattering cell (M) which is also used as viscosimeter reservoir. The end of the viscosimetric tube (A) must be inside the liquid, just above the scattering plane in order to avoid the scattered light reflexion on the glass and far away the beam. The B tube is used to establish the atmospheric pressure at the basis of the capillary and to fill the cell with a syringe needle (N). The pressure which allows the liquid to rise in the capillary is applied owing to the tube (C) which also contains a concentric teflon tube (P) used to exhaust the liquid out of the cell ; this inner tube is able to slide inside the outer one, keeping the air tightness. All the air inlets are connected through filters. The other parts of the viscosimeter set up have been described elsewhere.

3. Burette and thermostat

We have used an automatic burette (Metrohm) with a 20cm^3 content.

The circulation thermostat has been constructed with a platine resistor regulator (Haake thermosistor TP32) which allows a stability of 0.01°C.

4. General procedure

The whole automatization of the device is made possible and not too expensive by the recent development of the micro computers such as the PET Commodore, 32K octets, equipped with a output Bus IEEE 388 and working with basic language. It has several functions.

i) apparatus monitoring

- it operates the rotation of the optical system of detection by generating electric pulses transmitted to the stepping motor. The definition of the scattering angle is approximately 1/10°. The zero angle is first determined by observation of the maximum transmitted light through the slit (I, fig.2) when the prism holder is rotated ; then, the ajustable mark-index is set before the zero graduation drawn on the mobile cover. Two microswitches are trimmed in order to determine the beginning and the end of the run of the optical detection system.
- it commands the automatic burette according to a given dilution program

- it operates the air pump of the viscosimeter and controls the number of repeating measurements
- it can operate a magnetic stirrer if necessary
- in some cases, it may manage a temperature variation

ii) Data acquisition

- The photomultiplier 1P28RCA has a good response in red wavelenght. The output electric current is measured by a digital voltmeter Schlumberger (VH 2068) which is interfaced with the Bus IEEE 388 of the PET. Actually, we have not a control of the stability of the laser source but our experience shows that the drift of the light intensity during an experiment time (less than one hour) is neglegible. After each angle change, a delay is programmed before the computer takes the voltmeter informations and a new change is only operated when the stability of the scattered intensity is accepted by the PET according to the following programmed check : it is well known that intensity fluctuations are essentially due to the motion of dust present in the liquid, which always orginates an intensity excess. Thus, we can consider that the true value in a set of measurements is the lowest one. Our programm compares this lowest value for a set of u measurements with that obtained for the preceeding set of the same number of measurements. If the agreement is found to be better than 0,5% the computer gives the order of angle change.

- From the detection head of the viscosimeter, the flow times are measured by a electronic time counter which is also interfaced with the computer bus. The PET stores the values corresponding to each measurement.

iii) Data treatment

For light scattering experiment, we have written a programm to obtain M_w, R_G and the second virial coefficient A_2 by using classical least square procedures. The Zimm plot can then be drawn by a Hewlett Packard Plotter (7225A). The PET also calculates the intrinsic viscosity and the Huggin s constant. The numerical values of the different parameters are read on a printer.

B. APPLICATIONS

1. Light scattering with automatic dilution

The preparation of $10cm^3$ of a solution only is required to obtain the complete set of informations expected from light scattering experiments. : M_w, R_G and A_2. After determination and storage by the computer of the angular dependence of the pure solvent, contained in a classical cell, a given volume, $6cm^3$, of filtered and centrifugated polymer solution is introduced in the dilution cell and the scattered intensity is measured for a chosen angle selection. Instead of using magnetic stirring, we have prefered introduce, in the programm, a delay after each new addition of solvent. In fact, one observes that a perfect homogeneity of the solutions is still obtained after two or three minutes and the measurement for the first angle is only valided, if the test of stability is well verified.

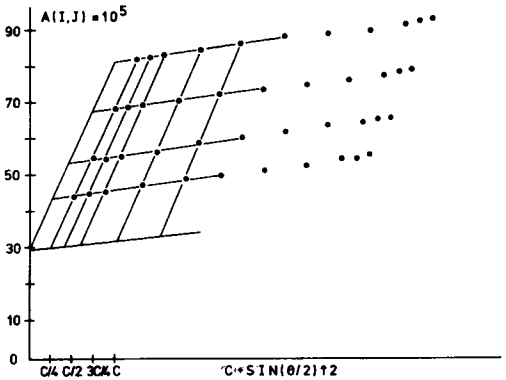

Figure 5 : Zimm Plot for PS (M_w=3.10^5)

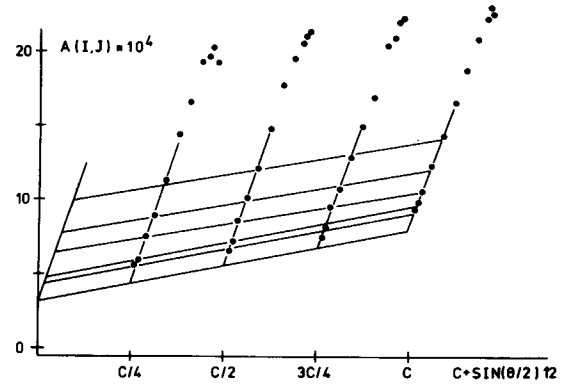

Figure 6 : Zimm Plot for PS (M_w=5.10^6)

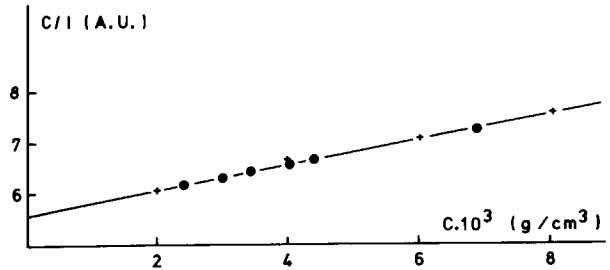

Figure 4 : (C/I)=f(c) at 90° for a low molecular weight PS sample : o automatic, x separate solutions

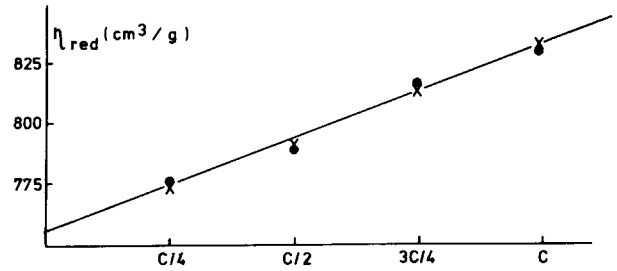

Figure 7 : η_{red}=f(c) for PS = 5.10^6 two different experiments

The device has been tested with polystyrene samples. On fig. 4, one can compare the variation of C/I 90° as a function of C, concentration for a low molecular weight sample (M_w=24000) either by using (o) or not (+) automatic dilution and there is no difference between the results obtained with the two types of measurements. The table I shows also the good agreement of the values obtained with automatic dilution with those determined by using a classical Fica apparatus (λ=4360Å and 5460 Å) for samples of higher molecular weights.

TABLE I

	λ [nm]	dn/dc	$M_w.10^{-6}$	$A_2.10^4$	R_G
Fica 50	436	0.111	1.37	2.81	717
	546	0.106	1.465	3.24	716
Our apparatus	632	0.1047	1.35	3.29	645
Our apparatus with automatic dilution	632	0.1047	1.39	3.27	635
Fica 50	546	0.111	1.1		
Our apparatus	632	0.1047	1.1		537
Our apparatus with automatic dilution	632	0.1047	1.09		575

On the two figures 5-6, are given examples of Zimm-Plots drawn by the plotter. The computer is able to select the convenient abscissa scale ($c+k \sin^2 \theta/2$) according to the calculated values of M_w and R_G. This representation allows the comparison between experimental points and their fits by least square analysis (straight lines).

We give here only a rough example of data treatment neglecting for a routine application more elaborated calculations.

2. Light scattering and viscosimeter coupling

A good thermostatation which is not very important for light scattering experiments become crucial for viscosimetric measurements. We have obtained, for benzene for instance, on a set of measurements, a relative stability of 2.10^{-4} on the flow time. The figure 7 represents the variation of the reduced viscosity with concentration for two different experiments. The Zimm-Plot obtained in the same experiment is that shown in fig. 6.

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