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Instrumental modifications for light scattering and differential refractometry at 633 nm

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A detailed description is presented of all the modifications necessary to enable the SOFICA light scattering photometer to be used with a He–Ne laser operating at 633 nm. Modifications of the Brice Phoenix differential refractometer for use at this wavelength are also given.

(Keywords: SOFICA light scattering photometer; helium–neon laser; Brice Phoenix differential refractometer; tungsten filament lamp)

INTRODUCTION

Of the relatively few different types of commercial light scattering photometer used to characterize polymers in dilute solution, the French-manufactured SOFICA instrument probably enjoys most widespread use. Both the standard model discussed here (SOFICA 42000) and the more refined version (FICA 50) use as the light source a high-pressure mercury lamp (SP 500 W), which must be water-cooled. Isolation of appropriate wavelengths *in vacuo* (λ_0) of 436, 546 or 578 nm is effected by filters. However, manufacture of these lamps by Philips (Holland) has been discontinued and, unfortunately, no other comparable lamps are available. The possibility of replacing the incident optics of the SOFICA instrument by a fairly low-powered He–Ne laser emitting light at 633 nm was investigated by Millaud and Strazielle[1]. These authors demonstrated by means of their excellent experimental results that this source is adequate for obtaining satisfactory light scattering data despite the reduced scattering at this elevated wavelength. A general outline of the optical modification was presented[1] and, indeed, this can be done in a number of ways. We consider it useful to pass on to the considerable body of users of this instrument the precise details, potential problems, mode of alignment, etc. In this respect attention is focused primarily on such practical aspects rather than application of the modified instrument for light scattering studies.

Because use of $\lambda_0 = 633$ nm necessitates that specific refractive index increments of polymer solutions (dn/dc) be known at this wavelength, we include also some comments on appropriate modification of the commonly used Brice Phoenix differential refractometer.

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PROCEDURE: SOFICA 42000 LIGHT SCATTERING PHOTOMETER

Optical modification

Figure 1 shows the unmodified instrument, the incident optics of which comprise: 1, Hg lamp; 2, anticaloric window; 3, total reflectance prism; 4, chromatic condensing lens; 5, filter; 6, glass diffuser; 7, iris diaphragm; 8, reference photomultiplier; 9, polarizer; 10, adjustable slit; 11, principal lens. With the exception of components 10 and 11, all of these are replaced by a He–Ne laser, indicated as item 21 in the upper part of *Figure 1*. Removal of the items shown within the broken lines in *Figure 1* renders many auxiliary components redundant, mainly those which service the mercury lamp, which can therefore also be removed. These include the cooling water lines, the diaphragm safety interlock switch, the fan and the large transformer situated at the rear of the instrument. Removal of all of these items leaves ample room for installing the laser and also makes the instrument much lighter.

We installed a 5 mW He–Ne laser (Melles Griot 05 LMHP 151) on a home-made laser mounting (*Figure 2*), which was basically similar in form to the commercially available Melles Griot cylindrical laser holder, model 07 HLH 002. To reduce the amount of laser lead protruding from the side of the instrument the incident block, which accommodates the variable slit, polarizers and filters, was removed (four bolts attached to the top plate) and the portion carrying the variable slit was cut away and replaced. The laser mount was bolted to the baseplate of the instrument and the laser was mounted with a vertical plane of polarization ensured by having the power cable protruding from the bottom. The mounting was constructed of mild steel and was sprayed with black matt paint to prevent tarnishing. Detachment of the large left-hand panel of the instrument is necessary only infrequently, viz. when installing the laser and when adjusting the alignment screws (see later) of the incident

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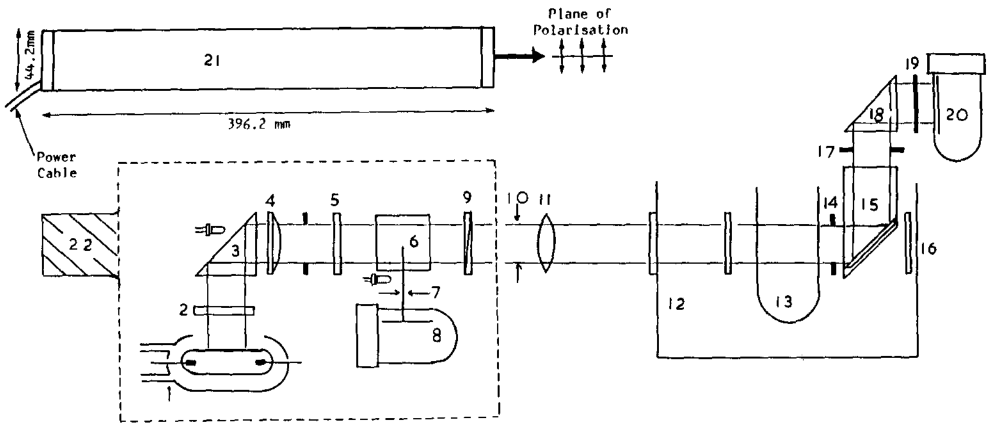

Figure 1 Schematic diagram of SOFICA 42000 showing sections removed (within the broken lines), laser replacement (21) and protective cage (22) for protruding portion of laser. Components 1–11 are explained in the text. Remainder: 12, vat; 13, cell; 14, entrance slit; 15, total reflection prism; 16, light trap; 17, exit slit; 18, second total reflection prism; 19, manual shutter; 20, photomultiplier tube for scattered light

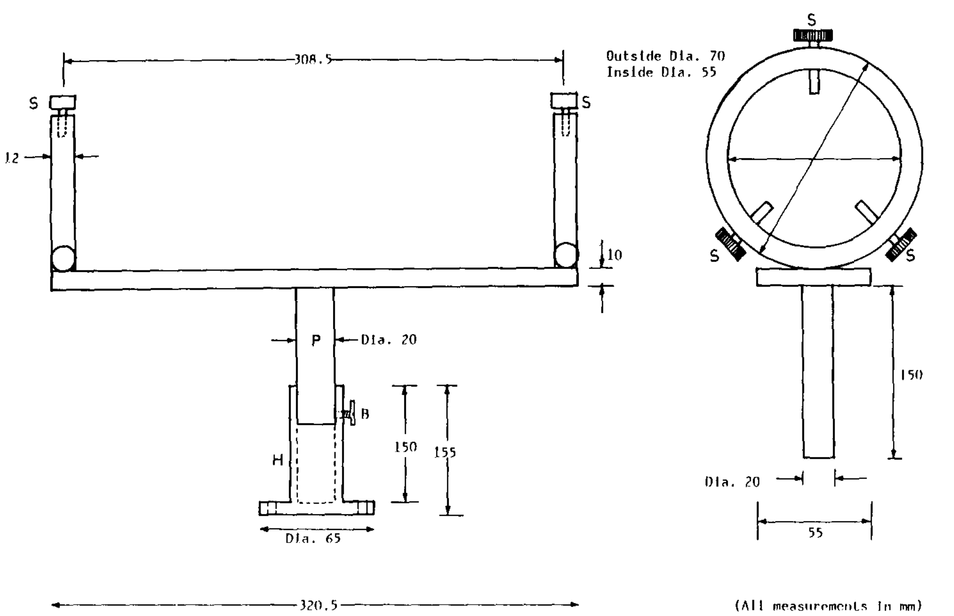

Figure 2 Side view (left and end view (right) of stand constructed to mount the laser. Adjustment screws are denoted by S. The height of the laser is adjusted by sliding the post P in or out of the post holder H and the final position is secured via the bolt B

optics. However, because of the length (~396 mm) of this particular laser, the panel could not be screwed back to the body of the instrument without first cutting away a small portion of the panel sufficient to accommodate the diameter (~44 mm) of the laser. To protect the protruding portion of the laser a mesh cage was constructed, placed round it and screwed to the panel, as indicated as item 22 in *Figure 1*.

Alignment

Incident optics. The vat is drained of solvent and the laser is positioned so that the beam passes directly through the centre of the vat. Precise alignment is accomplished by utilizing the first two of the following alignment devices, which are simple to construct:

(1) A circle of graph paper having its centre marked with a cross. This is mounted on a cylindrical piece of metal, the outside diameter of which is exactly the same as that of the recess in which the entrance window is mounted (*Figure 3A*).

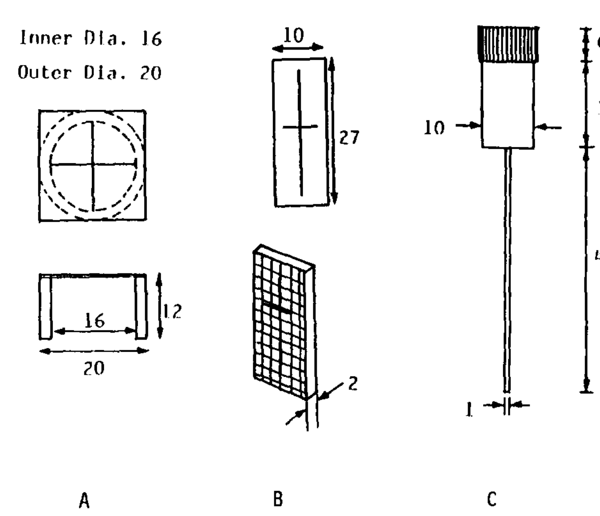

Figure 3 Devices A, B and C constructed for use in optical alignment of SOFICA instrument. All measurements are in millimetres

(2) A block of Teflon machined to the same dimensions as the light trap. One face of the block is covered with graph paper and the point that corresponds to the centre of the entrance window is clearly marked (note that this point is not the centre of the alignment tool) (*Figure 3B*).

(3) An alignment pin with a shank to fit the thermometer well hole (*Figure 3C*).

The beam is then adjusted (in our case using the three screws supporting the front section of the laser head) until the beam is centred on both of the above alignment marks in devices A and B of *Figure 3*.

After both conditions are satisfied, the laser is secured within its mount and the alignment is rechecked.

Scattered optics. Misalignment of the scattered optics is, in most instances, the cause of inaccuracy in the measured light scattering output and in extreme cases this is manifested by a pronounced downward bend in the lines of a Zimm plot at any particular concentration for scattering angles below $\sim 90°$. Alignment of the scattered optics is effected in the same way as that used for the unmodified SOFICA instrument. However, since the procedure is reported neither in the literature nor in the SOFICA manual, we present it here in the format of operating instructions.

With the high voltage switched off and the vat drained, the measuring photomultiplier housing is removed by loosening the two screws that secure it to the top of the scattered beam periscope. Remove the three screws that hold the goniometer plate ring in place and remove the ring. With the index finger through the sample hole, lift the goniometer plate straight up and out of the instrument. From the underside of this plate remove the cap screws that hold the black glass support and the thermometer well. Remove these items along with the thermometer well plug. Remove the slit collar from the prism by loosening the two set screws and slide the collar off. Replace the exit slit at the top of the periscope with the mounted graph paper (alignment tool A in *Figure 3*) and replace the goniometer plate. Turn on the laser and rotate the plate until the periscope lies within the 0–180° line. In this position loosen the two set screws that hold the periscope in place and rotate it until the brightest spot is observed through the graph paper. This spot should be centred on the graph paper. However, if this condition cannot be achieved, then the height of the air blade prism at the bottom of the periscope will have to be altered. The prism is held in place by a compression fitting and a nut. It is sometimes possible to adjust the height of the prism significantly by simply loosening the nut and repositioning the prism, but in the majority of cases the nut will have to be removed and shortened on a lathe to allow sufficient adjustment.

When replacing the prism in the compression fitting, the slits within the assembly must be aligned as the nut is tightened. This is achieved by observing the slits through the entrance face of the prism and rotating the prism until the edges of the slits line up exactly with the edges of the entrance face. The alignment of the scattered beam optics is accomplished by rotating the periscope until the beam is received in the centre of the graph paper, replaced by the exit slit. When this condition is satisfied, lock the periscope in place.

On completion of the alignment again remove the goniometer plate and replace the exit slit and align with the prism (same procedure as the used for aligning the slits). Slide the slit collar in place over the prism and, by observing the alignment pin C in *Figure 3* placed in the thermometer hole through the exit slit, rotate the slit collar until the pin is exactly centred in the slit. Lock the slit collar in place. Replace the light trap and thermometer pocket on the bottom of the goniometer plate. Replace the light trap (item 16 in *Figure 1*) at the back of the vat and replace the goniometer in the instrument. Replace the locking ring, its screws and the photomultiplier housing.

Fill the vat (item 12 in *Figure 1*) with a suitable immersion liquid such as mesitylene or toluene and check the alignment with a highly purified sample of benzene or toluene. The condition:

$$(I_\theta^v/I_{90}^v) \sin\theta = 1 \qquad (1)$$

should be obeyed at all angles θ. In equation (1), I_θ^v and I_{90}^v are the scattered intensities for the vertically polarized incident light at angles θ and 90° respectively. As seen in *Table 1* the symmetry and alignment for the modified instrument were excellent, the maximum deviation from equation (1) being only $\sim 1\%$ (at $\theta = 30°$). Good accord with accepted values was also obtained[2] with measured values of the Rayleigh ratio R_{90}^v of some pure liquids. In the present context it is not necessary to reproduce here exemplary forms of Zimm plot obtained with the modified instrument for standard polystyrene samples.

Electrical modifications

The removal of the incident optics necessitates the removal of the reference photomultiplier housing and tube. The reference photomultiplier measures fluctuations in the light source intensity and compensates for changes through a diode feedback system to the measuring photomultiplier tube. Owing to the stability of the laser light intensity this reference photomultiplier is not required and therefore to compensate for its function an external power supply is incorporated into the electronics which provides a constant variable voltage to the measuring photomultiplier tube. It should be noted that the high-voltage and detector circuit in *Figure 4* contains not only the present modifications but also amendments to some small errors present in the original diagram (*Figure 5.6* of SOFICA manual). The first part of the modification requires the removal of the Zener diode DZ68A, 56 kΩ resistor 0.5, 1.2 diode and 8 μF capacitor—see *Figure 4* (or *Figure 5.6* of SOFICA manual), and replacement of these components with a 15 kΩ resistor inserted on valve EF184 across pins 7 and 8; this resistor should be 2 W rated. This is an alternative

Table 1 Alignment data for scattering from toluene at 25°C and $\lambda_0 = 633$ nm

θ (deg)	$(I_\theta^v/I_{90}^v) \sin\theta$
30.0	0.989
37.5	0.999
45.0	0.999
60.0	0.998
75.0	0.997
90.0	1.000
105.0	0.997
120.0	0.998
135.0	0.999
142.5	0.999
150.0	1.000

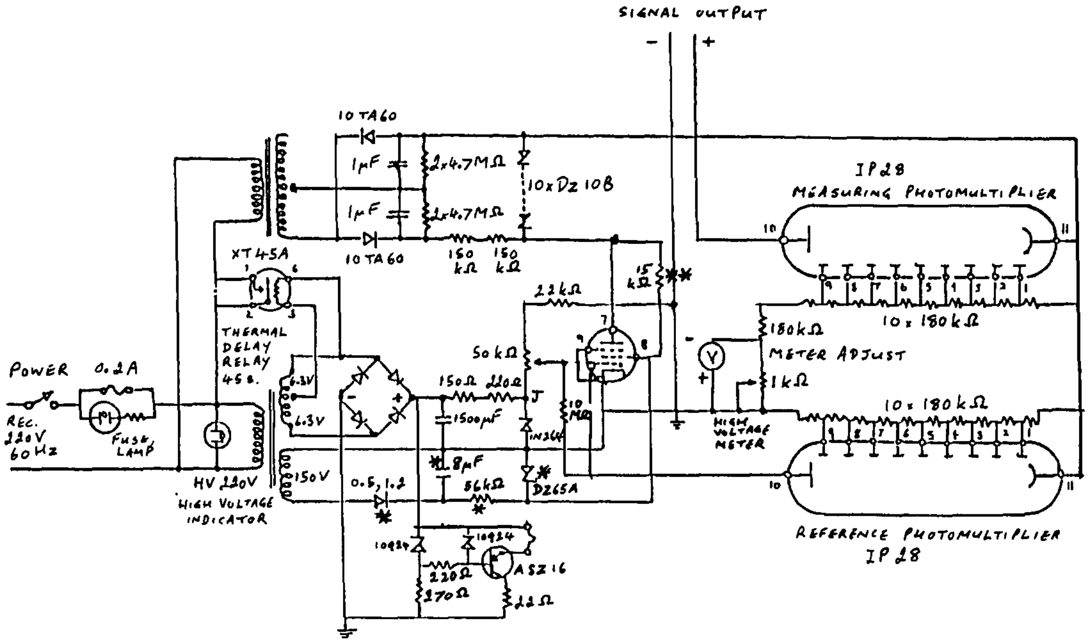

Figure 4 High-voltage and detector circuit. Components removed are indicated by * and the 15 kΩ resistor inserted is indicated by **

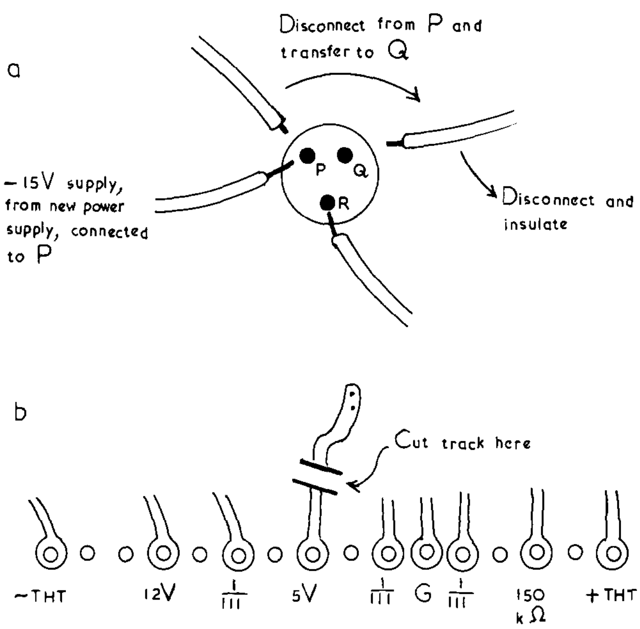

Figure 5 (a) Modifications effected at high-voltage control pot located on front panel; (b) printed circuit board

method of providing a reliable screen grid supply to the valve and gives improved stability. The modification is applicable to both the original Hg lamp instrument and the He–Ne laser one.

Secondly, and specifically to the laser-modified instrument, the reference photomultiplier tube is compensated for by connecting the positive side of a −15 V, 100 mA power supply to earth via the tag strip in the measuring electronic chassis. The negative side of this supply is connected to the pin P on the high-voltage control pot on the front panel, after first removing the grey wire as shown in *Figure 5a* and transferring it to pin Q. The wire removed from Q should be insulated and left disconnected. The wire on pin R is left untouched. Note that the nomenclature used here is not that which is used in *Figure 5.6* of the SOFICA manual. However for clarity it is emphasized that the grey wire (which is insulated and left disconnected) should be the one which connects to point J in *Figure 5.6* of the SOFICA manual. If the wires P and Q were transposed, one would have the situation of the pot operating in reverse, i.e. the high voltage going up when the pot goes down. Remove the printed circuit board from the right-hand electronic chassis (which has the variac on it) and cut a track as shown in *Figure 5b*.

Finally, the original measuring photomultiplier tube, EMI IP28 (item 20 in *Figure 1*) was replaced with a tube that was more sensitive to red light (Hamamatsu R446). The original photomultiplier tube could have been retained in principle, but has greatly reduced sensitivity to red light and would have yielded small and inaccurate light scattering output readings.

PROCEDURE: BRICE PHOENIX DIFFERENTIAL REFRACTOMETER

The unmodified instrument uses as light source a General Electric mercury vapour lamp type AH3 from which $\lambda_0 = 436$, 546 or 578 nm are isolated by filters. Isolation of $\lambda_0 = 633$ nm from this source is not possible. It is possible to use a small He–Ne laser in conjunction with optical fibres[1,3]. However, the modification described here is equally effective and is both simple and inexpensive. Reference should be made to *Figure 6a*.

In the unmodified form a right-angled metal plate P1 is attached to the end of the optical bench. The upper part of P1 contains a hole H1 for passage of the light through a filter in the filter turret also attached to P1. A protective hood, the mercury lamp, its socket and electrical leads are above the base of P1. All of these components are removed. A plate P2 containing a hole

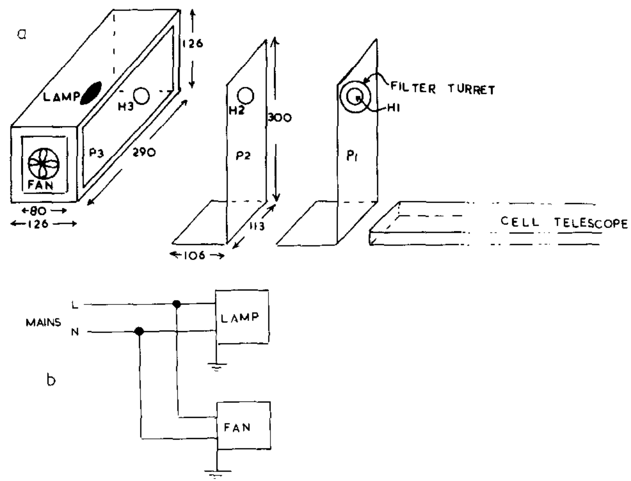

Figure 6 (a) Modification of Brice Phoenix differential refractometer and (b) relevant wiring of tungsten halogen lamp and fan (for explanation of P1, P2, P3 and H1, H2, H3, see text). All measurements are in millimetres

H2 is constructed and is bolted to P1, the new plate P2 being of similar dimensions to those of P1. A 500 W, 240 V tungsten halogen lamp (Radio Spares, West Germany, no. 566-099) mounted within a metallic case (Radio Spares, no. 566-033), which has a glass front window, is used as light source. The glass window was removed and replaced by an aluminium plate P3 containing a hole H3. To dissipate the heat developed, a 240 V fan (Radio Spares, no. 509-030) was bolted to one side of the metal case after first cutting out a 80 mm × 80 mm square from the side of the case. The electrical circuit was wired (*Figure 6b*) so that the fan and lamp could only operate simultaneously. A red glass filter (Oriel no. RG.610) was inserted in the original filter turret. This filter and the holes H1, H2 and H3 were all circular and of diameter 25 mm.

The modified instrument functioned well and, after calibration with aqueous KCl, gave values of d*n*/d*c* for polymer solutions at 633 nm which accorded perfectly[2] with those obtained via a Cauchy dispersion of values at lower wavelengths, which had been measured on the unmodified instrument.

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