Principles of Infrared Spectrophotometry

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ALTHOUGH THE INFRARED FIELD was later than either ultraviolet or visible in having a commercially available spectrometer, it is now in a peculiar position with respect to spectrophotometry. In this article spectrophotometry implies the automatic comparison of the spectral power in two radiation beams—an I_o, or reference, beam and an I, or sample, beam. Whereas ultraviolet and visible together have only two types[1] of commercially available spectrophotometers, infrared alone has two, and a third one is under consideration. All three types are different in basic principle.

None of these types is original with the manufacturer—two, at least, were known before commercial production begun. One would therefore conclude that no principle is completely superior to the others—that each has certain inherent advantages and disadvantages whose relative weights influenced the makers' choice. Under such circumstances, a potential user must consider the implications of each principle very carefully in studying the performance of the various instruments. The advantages and disadvantages of the principles are not readily apparent in a description of the instruments alone, primarily because infrared techniques are applicable to such a wide range of problems.

The three principles of infrared spectrophotometry may be described as the memory standardization, the optical null, and the direct ratio. It is not the purpose here to give more than very brief descriptions of the methods, since full detail is available in the literature or from the manufacturers.

System A. *Memory standardization* (*1, 2*). A single beam instrument is used, and an I_o spectrum is run. A chosen characteristic of the I_o run is recorded and played back during the I (sample) run to provide the comparison. In the Beckman instruments, the slits are servo-operated during the I_o run to give a constant radiation signal. The slit schedule is recorded on a magnetic tape, which is played back to control the slits for the I run.

System B. *Optical null* (*3–7*). Two separate radiation beams are taken from the same source, split in space, rejoined at a 180° rotating sector mirror, and passed through the spectrometer proper on alternate half cycles. The sample is placed in one beam, and a balance cell, if required, in the reference beam. If the radiation from the sample beam is different from that of the reference beam, an a.c. signal results from the detector. This signal is used to drive a wedged diaphragm in the reference beam to restore radiation balance or optical null. The position of the diaphragm is recorded continuously as a comparison of the two beams.

System C. *Direct ratio*[2] (*8, 9*). Again two radiation beams, reference and sample, are taken from the source, but essentially 90° radiation-chopping is employed—i.e., each beam is measured with shutter in and shutter out. The two net radiation signals that result from the detector are obtained separately. The I_o electrical signal is placed across the slide wire of a recording potentiometer, and the I signal is fed at the conventional point, so that an automatic ratio of the two signals is obtained.

Comparison of the three systems is presented in Table 1. Instrument characteristics are shown in the left-hand column. Plus and minus signs are used merely to show with which method the advantages seem to lie. It is emphasized that these are advantages in principle only, and not in performance of the instruments available. It may well occur that a manufacturer, at disadvantage in a certain characteristic, may solve the problem so successfully that his performance in that regard may be superior to the others.

With reference to the first two characteristics of Table 1, comparison is based on single-beam a.c. operation as unity in each respect, although the single beam does not give results equivalent to the beam comparison systems. The noise to signal comparisons are only approximate; actually, even with the assumption of instantaneous detector response, there is a small difference between the instruments of references (*8*) and (*9*) of system C. In reference (*9*) there may be some further signal loss as a function of detector response because of the complete 90° on-off chopping. Similarly, the signal of system D can be more than twice the standard chosen. In system A the noise varies from the $\sqrt{2}$ to 1 from 100–0 per cent

[1] An instrument supplied by the Applied Physics Laboratories for use in ultraviolet or visible is based on a different principle from the General Electric visible spectrophotometer.

[2] In the Savitsky conversion, the radiation beams are not widely separated in space, so that sampling restrictions are involved. This is not considered in the general arguments given here, since it is not inherent in the principle.

TABLE 1

COMPARISON OF METHODS OF INFRARED SPECTROPHOTOMETRY

Requirements or characteristic	System A (memory standardization)	System B (optical null)	System C (direct ratio)	System D (single-beam d.c.)	Standard (single-beam a.c.)
1 Noise	$\sqrt{2}-1$	1	$2\sqrt{2}-2$	½	1
2 Recording time	$2 \rightarrow 1$	1	1	1	1
3 Net radiation measured	+	−	+	−−	+
4 Amplification	−−	++	+		
5 Source stability	−−	+	+		
6 Optical	++	−−	−		
7 Atmospheric interference	−	+	+		
8 Slit mechanism	−	+	+		
9 Sampling	+−	−+	−+		
10 Elasticity (double beam)	−	+	+		
11 Elasticity (single beam)	+	−	−		

transmission, because two independent signals are compared. In system B the noise is unity, provided the filtering blocks noise frequencies greater than the response time of the servo-balance system. The noise of C is twice that of A, since the radiation is measured only half the time. For single-beam d.c., the noise-to-signal ratio is about ½, or somewhat less, since total radiation is used. For one spectrum the recording time for system A is twice that of the single beam standard, because unit time is required for the I_o as well as the I run. However, the time factor of two can approach one if instrument conditions are maintained constant, so that a single I_o run can be used for many I runs. In B and C the recording time is unity. Row one can be converted to unity if the values of row two are multiplied by the square of the respective noise values. Under normal conditions of spectral recording and instrument variation, the factor of $\sqrt{2}$ in noise is probably not appreciable. However, the noise increase of system C will probably be noticeable.

In system B the net radiation is not measured. It is assumed that the source zero radiation condition is the same in either beam, and an explicit zero radiation value is not measured. This assumption is valid if the sampling temperature condition in each beam is approximately the same as the detector temperature. Although this is true for normal work, system B would give slightly erroneous results for liquid-air or high-temperature samples. The error could be measured independently and a correction applied, but in so doing the time advantage of the system is lost. In system D the radiation zero can be measured only at the beginning and end of each spectral region and must be assumed in between. This disadvantage more than balances the noise advantage of the system for most purposes and is the reason d.c. recording is not commonly used today. The lack of a net radiation measurement also implies that the I_o signal is not available for servo-control of operating variables such as slit width, speed of recording, or electrical filtering.

The requirements on amplifier linearity and gain stability, as well as source stability, are very stringent in system A. These characteristics must be maintained very accurately over a period of one-half to one hour for a single spectrum, and for considerably longer if one I_o run is to be used successively. In system B the amplifier has only to detect a null. Similarly, the source must maintain appreciable stability only over a time long compared to the sector-mirror period. In C, amplifier linearity must be good, but gain and source stability conditions are the same as for B. The linearity requirement could be eliminated if the system were operated on an electrical null condition before the amplifier and the ratio of the bucking signals obtained.

In optical requirements the situation is reversed. All the advantage lies with system A. In systems B and C, where split optical paths are used, reflection and scattering characteristics must be maintained constant in each beam. This is very difficult because of the nature of infrared transmitting windows and the number of octaves in the spectral region. System B has an added disadvantage over C in that, for both transmission accuracy and reproducibility, the balance comb or wedge must be accurately linear, and the radiation distribution across it must remain uniform and constant. If the comb is placed at a point conjugate to the source, radiation distribution over the source must remain constant, and there is necessarily a very small but unavoidable error as a function of slit width at very low transmissions. At such a position it is also conjugate to the slits, which introduce dangers from slit jaw irregularities and diffraction effects at very small slit widths. If it is placed at an aperture stop, the reflecting surface of all collimating or condensing mirrors must stay uniform.

In fact, the reversals of advantages 4 and 5 versus 6 are probably the greatest weights in the manufacturers' choice, and considerable experience will be required to decide the validity of the choice.

If atmospheric interference is present, the advantage is with B and C. Careful optical alignment is required to eliminate these effects, but once it is achieved, it is independent of atmospheric changes. This also eases the instrument desiccation problem considerably. In system A atmospheric interference changes imply a new I_o.

The requirements on the slit mechanism are also more stringent in A than in B or C. The slit schedule in A must repeat accurately from I_o to I run, whereas in B or C it must be held only close enough to maintain reasonably constant I_o energy and not change the resolution appreciably.

In sampling, the advantages are mixed and often depend on the nature of the work. For gas or dilute solutions the same sample cell can be used in both I_0 and I runs in system A. The time factor for the two runs must be considered. If the sampling is repetitive, the advantage is clear. If the sampling is highly varied, systems B and C would require the same time to make a blank run as system A requires for the I_0 run. However, if the blank run shows that correction to the sample run is required, such a correction is not automatic and may be very tedious. If the blank runs are not necessary as a correction, the time advantage is with B and C. For pure liquid runs, the blank is not the empty cell but a single double thickness plate. Here the advantage is with B and C, unless a large number of runs is involved. In the one case of differential spectra, where one wishes to balance out a component present to 95 per cent or less, system A is at a disadvantage in varied work. Under such conditions the same cell cannot be used, because the component to be balanced will not have the same net thickness in each case. The thickness difference can be made up by a material that has no absorption, but this is possible over only limited spectral regions. The use of cells of different thickness is difficult, particularly if the net thickness contribution of the component to be balanced cannot be controlled—i.e., balancing out the major component of an unknown to study the minors. Such cases are best handled by use of a variable thickness cell in the reference beam and by study of several absorption bands of the major to determine the best compensation thickness. Adjustment of the cell in system A for an unknown sampling would require multiple measurements of I_0 and I values at the absorption points.

The double beam elasticity—i.e., simultaneous beam comparison—of systems B and C is the advantage that is involved in the last point of differential sampling. This advantage is also apparent in a case where a spectrum is scanned with a given set of instrument variables, say, for a survey run. If a certain region is desired under different trial conditions, systems B and C can be reset immediately. System A requires changing the I_0 tapes or perhaps running new ones. On the other hand, systems B and C lack single-beam elasticity. The requirement that the split optical portions remain matched precludes ease of special work, such as changing the sample beam for some particular problem.

These would seem to be the major comparisons in principle among the three systems. It is also of interest to compare certain of the design features of the Beckman memory standardization instruments and the Perkin-Elmer optical null instrument. Each has provided a rather wide range of control of the various operating variables, as well as camming systems to furnish spectra linear in λ, ν, etc. Beckman has made the scanning speed proportional to the slit width and has chosen to servo the slit widths in the I_0 run to provide a constant energy signal versus wavelength. This slit schedule is repeated in the I run. Perkin-Elmer provides a speed suppression feature that permits partial control over scanning speed as a function of radiation beam off balance. Essentially, the mechanism provides a scanning rate as set for regions of no spectral absorption, and automatic slowing of the rate where absorption bands are present. For the slits, Perkin-Elmer has chosen a series of slit-width schedules which provide reasonably constant I_0 energy to the servo, and which differ from each other by successive factors of $\sqrt{2}$. Again, once these design features are set, comparisons in principle are possible, although the resultant spectral effects must be studied experimentally for any decisions.

The Beckman rate of scan feature is very attractive, since it provides automatically controlled, optimum rate of scanning for information that may be present in each spectral region so long as I_0 versus λ is a reasonably smooth function. The Perkin-Elmer suppression, on the other hand, permits some speed discrimination, dependent on whether the information in a region is of interest. A combination of the two features would be highly desirable. A decision between each alone is difficult, unless they could be compared on the same instrument. The Perkin-Elmer feature is more apparent for rapid scanning and loses its effectiveness at slower scanning rates. The Beckman scanning method would ensure the same scanning time on either a wavelength or wave-number basis. This, combined with the decision to servo the slits, makes their prism interchange easier in principle, since Perkin-Elmer must interchange both slit and wavelength cams, whereas Beckman must change only the wavelength cam.

The Beckman decision to servo the slits implies the disadvantage in solution runs that the spectral resolution schedule for a solute would be a function of the solvent thickness used, since the I_0 slit schedule would vary with solvent thickness. A chemical mixture is often more soluble in a given solvent than its pure components. Minimum solvent thickness is usually desirable, but it might be difficult to obtain pure spectra under the same solvent slit schedule as would be desired for the mixture. Similarly, there would be a change in resolution schedule in the Beckman with appreciable atmospheric absorption. A similar effect might be observed in the Perkin-Elmer with rapid scanning, as strong atmospheric absorption would alter the gain in the servo loop and make the response sluggish. In the water region, at least, because of the narrow band widths, these effects would not be noticeable in either system with normal samples.

Each instrument seems to be at a disadvantage in differential spectral running where one wishes to obtain a valid spectrum of a solute in a spectral region of high solvent absorption. In the Perkin-Elmer the desired slit-width schedule is chosen and the amplifier gain increased, so that the product of available I_0 signal times gain is sufficient for the servo system. To reduce the noise resultant from the high gain, the instrument response time must be increased and scanning speed must be reduced to permit following the spectral structure. With the scanning speed so set, the instrument is operating inefficiently in the regions of high solvent transmission, since it is running more slowly than necessary.

The same situation holds in the Beckman. With a certain resolution desired at the bottom of a solvent band, the energy available is fixed and, therefore, the signal value by which the slit program is determined. In regions of high solvent transmission the slit must narrow to maintain this constant. Since scanning rate is a function of slit width, the instrument will scan more slowly than necessary through the latter regions, although spectral resolution would be increased.

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Comments on "Principles of Infrared Spectrophotometry"

VAN ZANDT WILLIAMS very kindly submitted a draft of his paper to us for comment prior to publication. Although in many respects we have come to full agreement with Dr. Williams, and we appreciate and respect his sincere effort to present a judicial consideration of the instrument problem, there remain certain irreconcilable differences in point of view between us.

One such issue concerns the respective time and noise efficiencies of the instrumental systems. A spectrophotometer is used to collect data. Whether these data are truly "per cent transmission" can only be determined by making a standardizing run as well as a sample scan, as Dr. Williams recognizes in his discussion of the sampling problem. The true per cent transmission is the quotient of these independent values, hence "noise" in both runs contributes to errors in actual values of per cent transmission. Furthermore, to be accurate, data must include matching corrections. These considerations are valid for any spectrophotometric system used in any wavelength region. In the infrared, however, they are of unusual importance, because of the magnitude of the noise problem and the impermanence of common optical materials.

The distinctions between systems A and B in respect to noise and recording time are therefore these: records made with system B do not contain the standardizing information and, consequently, may have lower noise, but they represent per cent transmission only approximately. System A provides a slightly "noisier," but direct-reading, record. Any method that can be proposed for modifying system B to provide actual per cent transmission records increases its noise level. Also, in principle, to obtain equally reliable per cent transmission data with either system, the same number of scans is required. The application of these ideas to the other systems is obvious.

The problems of amplifier linearity and stability and of source stability are admittedly important for system A. We feel, however, that even greater emphasis should be placed on the alternative difficulties encountered in system B in obtaining linearity and achromatism of the beam attenuator. We also feel that it is relevant to point out that the required high order of amplifier stability and linearity and of source stability can be obtained by straightforward application of recognized techniques in electronic engineering. Fortunately, stability and linearity need not depend upon nice mechanical adjustment or perfection of construction of components, but may be inherent in design. The validity of these statements has been tested in a commercial infrared spectrophotometer for almost five years.

Another significant distinction between system A and those remaining is that the former requires far more precise control of monochromator temperature, in order to achieve the extreme wavelength stability needed to retain compensation of sharp background absorption bands at high resolution. Experience has shown that this difference is of considerably greater importance than most of those formerly emphasized.

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