Computer Aided Spectroscopy[1]

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Abstract

Techniques are being developed which have as their objective improvement in the accuracy of infrared absorbance measurements and more exact recording of the true band shapes. From these improved spectra, accurate quantitative parameters are being obtained which can supplement or even supplant the present chart recordings as the fundamental spectral representations. These techniques include methods for processing spectra to eliminate most of the instrumentally introduced artifacts and to resolve the corrected spectra into algebraic representations in the form of sums of distribution functions. The consequences of the increasing use of these techniques will be to improve significantly our ability to do both qualitative and quantitative analysis.

Introduction

For the past few decades, the progress of analytical chemistry has been associated with the development and exploitation of various black boxes. These black boxes, the various emission and absorption spectrometers and the chromatographs, have made it possible for us to delve deeply into the structure of matter and to more exactly define its composition. We now have a new black box, the digital computer. This one, however, is of a different kind. It transcends the specific analytical techniques and has application to all areas of analytical chemistry. In a sense, it is a black box for the other black boxes.

It is not difficult to devise uses for the digital computer in analytical chemistry; in fact, many of us have used one for the calculation of standard deviations or perhaps for an analysis of variance or for the fitting of a curve to calibration data. What I intend to describe, however, is a more intimate union between the computer and analytical instrumentation and, more particularly, the results and future promise of the union of a digital computer with an infrared spectrophotometer.

Procedures

Interfacing

While one can transcribe points from an infrared spectrum into punched cards to be entered into a computer, it is much easier to punch the cards or paper tape directly. Several devices to do this have been described; for example, the card system described by Rawlins and Shore (11), or the paper tape system reported by Peterson et al. (8). An even better system, however, is to have the digital computer read the data directly as the spectrum is being scanned. Ordinarily one does this by equipping the spectrophotometer with a pair of encoders mounted on the wave number and transmittance drive shafts. These encoders are read, decoded and translated into computer legible numbers by an interface unit which also provides the timing pulses which direct the computer to read the points at controlled intervals.

Fig. 1. Interface hardware for four infrared and ultraviolet spectrophotometers.

The interface hardware used in our laboratory for a system of four infrared and ultraviolet spectrophotometers is pictured in Fig. 1. This system is composed of four modified Perkin-Elmer encoder readouts which are wired directly to the encoders and to an IBM 1800 computer. The digitizers allow us to control the digitizing rate in steps, starting at one point per 10 cm^{-1} to a maximum rate of one point per 0.1 cm^{-1}. Associated with this installation is a typer-printer through which the analyst can communicate with the computer, directing it to process the acquired data by any one of several stored programs. The analyst uses the keyboard to transmit such information as sample identification, cell number, and sample weight and type, as well as to communicate the choice of calculation method.

While the details of the interface units are interesting enough, of more concern here is what is actually done with the numbers, what we can expect to do in the future, and, furthermore, how this can be of use to the analytical chemist.

Instrument Calibration

What we would like to do is to insert the sample into the spectrophotometer press the start button,

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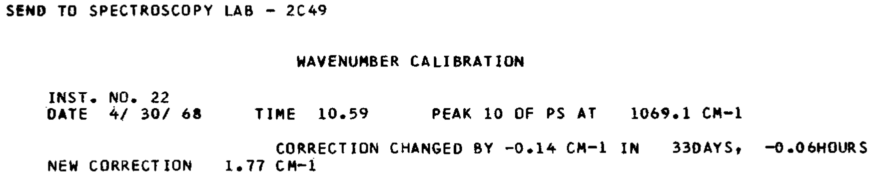

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SEND TO SPECTROSCOPY LAB - 2C49

                         WAVENUMBER CALIBRATION

    INST. NO. 22
    DATE  4/ 30/ 68     TIME  10.59      PEAK 10 OF PS AT   1069.1 CM-1

                   CORRECTION CHANGED BY -0.14 CM-1 IN   33DAYS,  -0.06HOURS
    NEW CORRECTION   1.77 CM-1
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FIG. 2. Computer printout of the results from a wave number calibration run.

enter the sample description into the typer, and, a short time later, have the computer print out a complete qualitative and quantitative analysis.

In order to do this, we need to provide means for accurately calibrating the instrument wave number and transmittance scale, determining the cell thickness and correcting the observed spectrum for errors introduced by the finite slit width and by the dynamic response of the spectrophotometer.

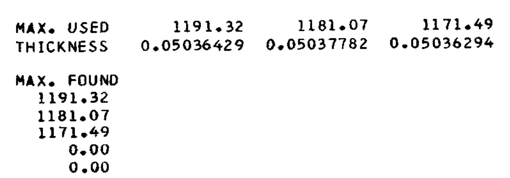
Wave number calibration is not so difficult. In practice, we set the instrument to scan an absorption band of a standard, such as polystyrene or indene. The computer is then directed to locate the transmittance minima, to compare them to tabled values of the true positions and to compute wave number corrections. These corrections are stored in a table in computer memory and referred to whenever wave number correction is required. A computer printout from such a calibration scan of a single polystyrene band is shown in Fig. 2. The next step is to have the computer fit the correction data from the table to an equation and then use the equation to produce a point by point correction of the spectrum.

Transmittance scale calibration is most effectively accomplished using the rotating disks devised by Jones (4). These rotating disks are accurately calibrated by photogrammetry and have provided transmittance calibrations to 0.2%. The calibration data for the transmittance scale can be used to correct observed transmittance readings in the same manner as is used for the wave number correction.

With the wavenumber correction known, one can determine the thickness of an absorption cell from its interference pattern in the conventional manner using the computer to locate fringe maxima and to perform the calculations. We have chosen to use a short method devised by Burrill (3) which completes the calculation after locating only three fringe maxima. The maxima are located using a modification of the smoothing and differentiating technique described by Savitzky and Golay (13). The printout from this procedure is shown in Fig. 3.

The effect of the finite slit width is to degrade the resolution of the spectrometer, the spectrum obtained having bands reduced in intensity and increased in width over that to be expected from the instrument dispersing element and optics. A method for reducing the effect of finite slit width has been described by Jones and co-workers (5,6). In this procedure, a spectrum with improved resolution is obtained by a successive approximation method termed "pseudo-deconvolution."

The dynamic error observed in a spectrum is caused by the time delay introduced by the finite time required for the spectrometer to respond to the change in signal level. This time delay depends on the rate at which the signal is changing and is not simply a displacement of the total spectrum. The response of a spectrometer to a sudden change in signal level, such as is produced by rapidly removing a total absorber from the sample bean, is shown in Fig. 4. Appropriate mathematical analysis of this response curve (7) yields a response function for the spectrophotometer which is plotted in Fig. 5. This response function, of course, will vary with instrument settings and can be interpreted as the attenuation and time shift produced by the instrument in a signal which is changing with the given frequency. For example, the figure indicates that if the interference pattern of a cell were scanned so that one cycle or fringe were completed in one second, the



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SEND TO SPECTROSCOPY LAB - 2C49

                          CELL CALIBRATION

CELL 10   DATE  4/ 30/ 68   11.29 HOURS   INST. NO. 22

  THICKNESS   0.05036834  +-  0.00000631 CM.

  CHANGE      0.00056134  IN  32 DAYS

  CORRECTION   1.63 CM-1 AT 1181.4 CM-1

  MAX. USED      1191.32     1181.07     1171.49
  THICKNESS   0.05036429  0.05037782  0.05036294

  MAX. FOUND
    1191.32
    1181.07
    1171.49
       0.00
       0.00
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FIG. 3. Computer printout of the results obtained for the determination of sample cell thickness.

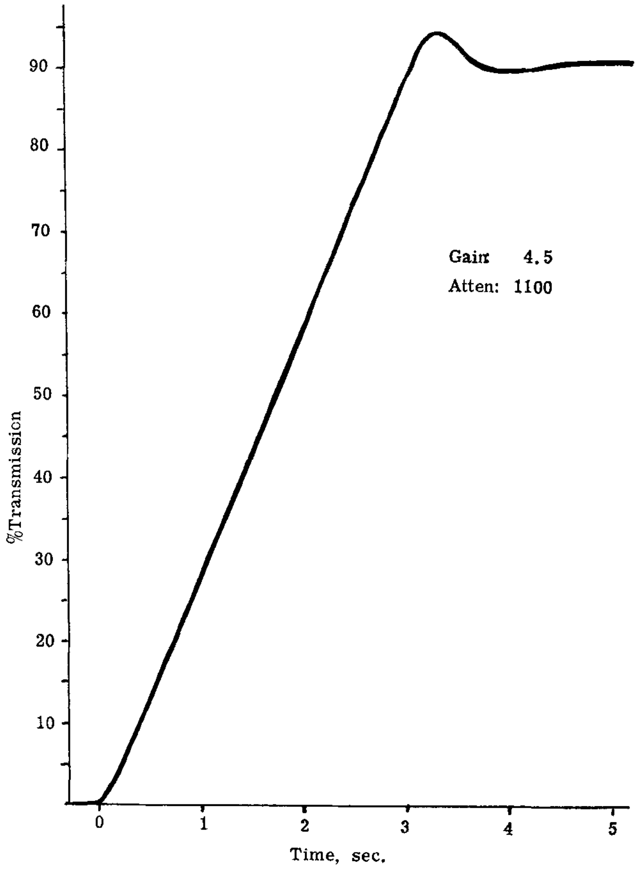

FIG. 4. Response of an infrared spectrophotometer on abrupt removal of a total absorber from the sample beam.

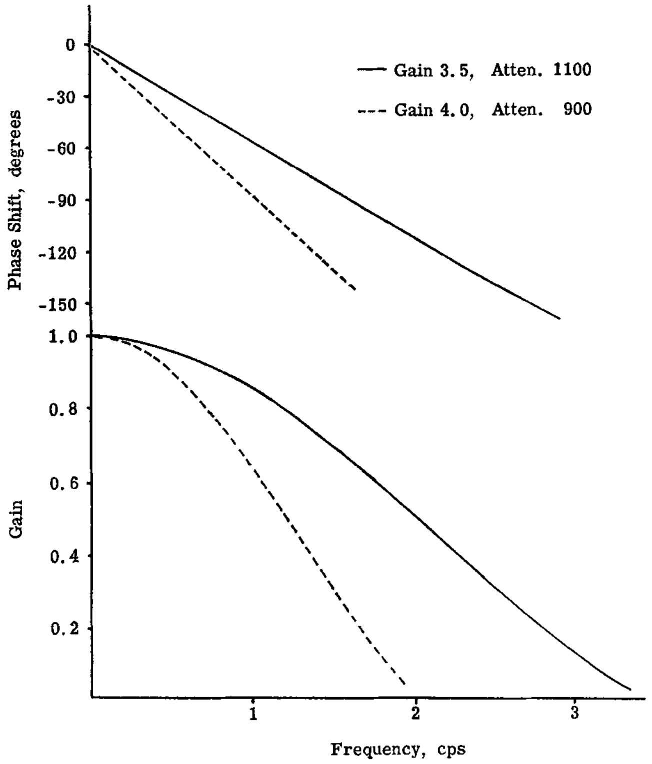

FIG. 5. Response functions calculated from the response of the spectrophotometer at two instrument settings.

curve would be only 0.9 times its true amplitude and would be shifted by 50/360 of a second.

Now, any infrared spectrum can be represented as the sum of a series of sine waves of varying frequency and amplitude. The effect of the response function is to attenuate these sine wave terms and to shift their phase. Results which could be expected on a Gaussian shaped band are shown in Fig. 6. The dynamic effect has caused a reduction in intensity, an increase in half width, and the introduction

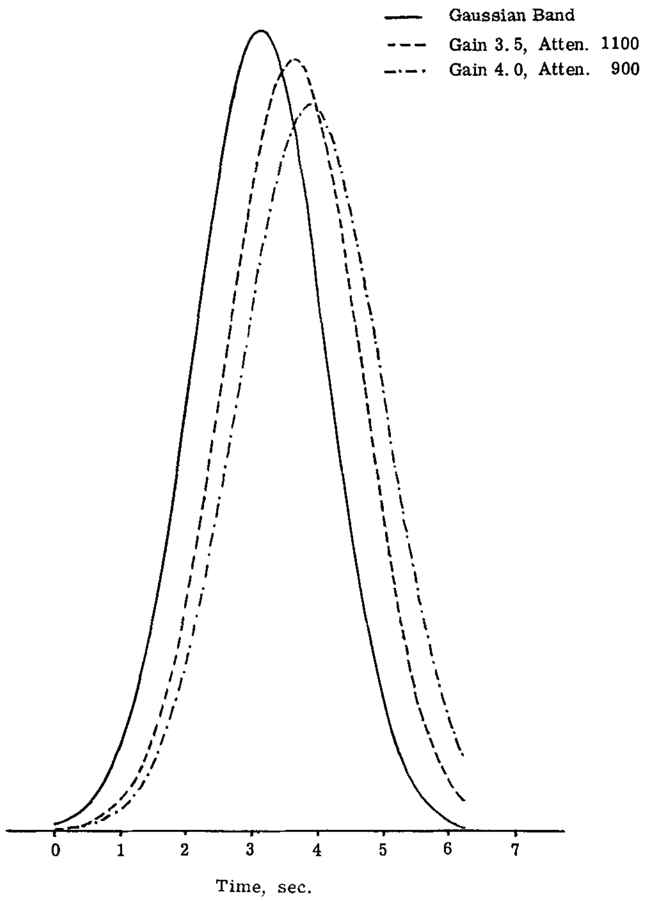

FIG. 6. Calculated effect of instrument response functions on Gaussian absorption band at two instrument settings.

of a definite asymmetry. Similar effects can be observed in spectra as can be seen in Fig. 7 which is a portion of the cyclohexane spectrum scanned under three sets of instrument conditions.

Correction for the dynamic error can be made using

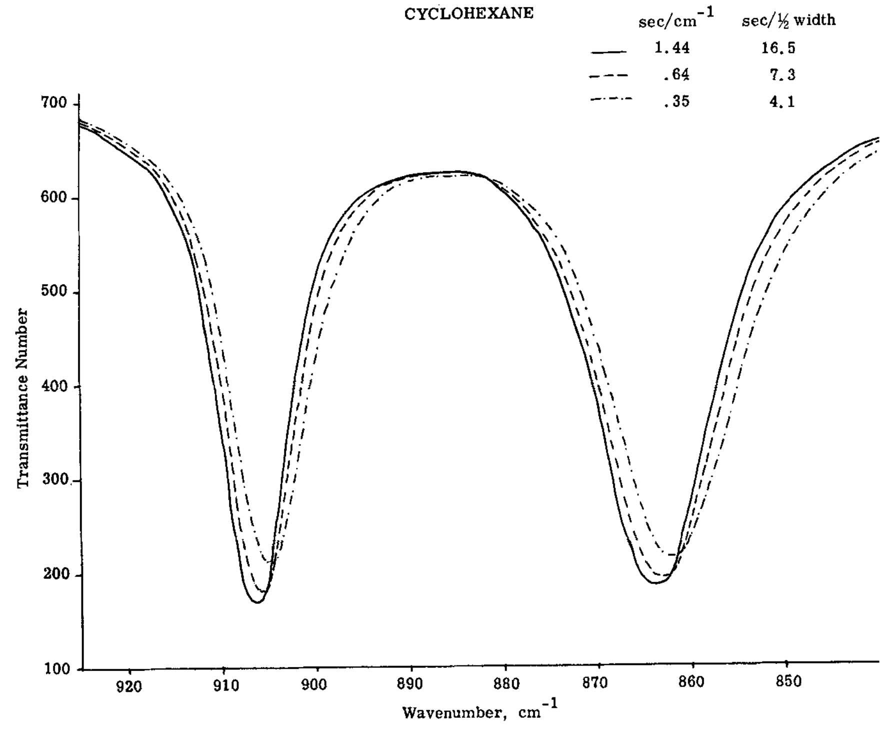

FIG. 7. Observed effect of instrument response functions on cyclohexane bands at two instrument settings.

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                SEND TO SPECTROSCOPY LABORATORY - 2C49 ITC

SAMPLE NUMBER                                            DATE  3/26/68
                                                         TIME 21- 1
DETERMINATION OF AMIDE                                  CELL      4
                                                         THICK.   0.0471
                                                         INST.NO.     22
    COMPONENT     PERCENT
    FREQUENCY   1618.0   1592.0    1517.0
    ABSORBANCE   0.100    0.173     0.055
    D E AMIDE       0.347
    M E AMIDE       1.073
    AMM AMIDE       0.212
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FIG. 8. Computer printout of the results obtained for the determination of amides in a detergent product.

the mathematical techniques of the Fourier Transform; however, this has not yet been worked out in an efficient manner.

Data Reduction

Presuming that we can now produce an accurately corrected infrared spectrum, one which is independent of instrument conditions, we must consider what we wish to do with the numbers. A complete spectrum can contain more than 35,000 points, severely taxing the capacity of most computers. We wish to select, therefore, only those features of the spectrum which are important to the problem at hand.

We might want to perform a quantitative analysis. We can have the computer sort through the spectrum to locate specific absorption maxima and minima, make baseline corrections, and enter these into a set of simultaneous equations to perform a multicomponent analysis. Such an analysis for a three-component amide mixture in a synthetic detergent is illustrated in Fig. 8. For this method, the calibration data were also determined by the computer from standard samples of known composition and stored in memory to be retrieved when required for this analysis.

At the present time, we have most of our quantitative methods on the computer. A collection of general purpose programs allows the choice of analytical wave lengths and methods of calculation. The analytical conditions are stored in the computer memory in tables and are referred to by the stored programs when the specific methods and sample descriptions are entered by the analyst.

Qualitative Analysis

For data storage and retrieval purposes, what we would like to do is to take the inked line from the graphical spectrum and wad it up in such a way as to eliminate the blank paper yet be able to regenerate the graphical spectrum at any time. One way to do this is to find an algebraic function which would fit the spectrum. We could then use the parameters from the algebraic equation as a description of the spectrum in much the same manner as one represents a calibration curve by the linear equation which fits it, using the slope and intercept as parameters.

Sophisticated procedures for doing this have been reported by Pitha and Jones (9,10), and by Bell and Biggers (2) using the methods of "non-linear least squares" and fitting the spectra to sums of Voigt distribution functions. The result of these procedures is a table of parameters that are related to the peak position, peak height, and half width and which are a complete quantitative representation of the original spectrum. This table of parameters can be used to regenerate the original spectrum from the computer or to generate absorbances for use in quantitative analysis. Of greater interest, however, is the potentiality for qualitative analysis.

I would like to mention briefly three qualitative analysis procedures which are now made possible or improved by the techniques described above and the further use of computers.

The first of these is the ASTM IBM punched card system. Fed with accurate quantitative parameters which add the dimension of peak intensity and using the powerful sorting techniques, such as those described by Anderson and Covert (1), we will surely attain considerable improvement in speed and capability of this system.

A second type of spectrum identification, useful for a limited subset of reference spectra, is the correlation method described by Reid and Wong (12). Using the normalized vector dot product as they did, or the more complex statistical correlation coefficient as criteria of similarity, spectral matching can be performed easily and automatically.

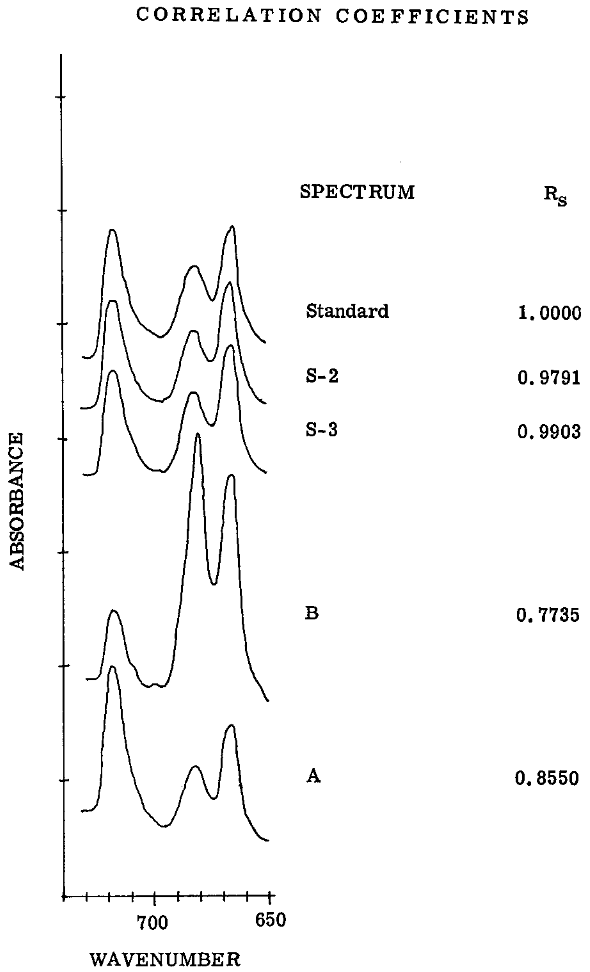

FIG. 9. Correlation coefficients obtained between five spectra.

The algorithms used for calculating the vector (R_v) and statistical (R_s) correlation coefficients are:

$$R_v = \frac{\sum\limits_{i=1}^{n} A_i B_i}{\left[\sum\limits_{i=1}^{n} A_i^2 \cdot \sum\limits_{i=1}^{n} B_i^2\right]^{1/2}}$$

$$R_s = \frac{\sum\limits_{i=1}^{n} A_i B_i - \sum\limits_{i=1}^{n} A_i \sum\limits_{i=1} B_i/n}{\left[\sum\limits_{i=1}^{n} A_i^2 - \sum\limits_{i=1}^{n}{}^{2} A_{i/n}\right]\left[\sum\limits_{i=1}^{n} B_i^2 - \sum\limits_{i=1}^{n}{}^{2} B_{i/n}\right]^{1/2}}$$

where A_i and B_i are the corresponding absorbances or transmittances at wave number i, and n is the number of points in the spectrum. These coefficients are normalized so that a perfect match between spectrum A and B are indicated by a value of 1.0; furthermore, the coefficients are independent of the amplitude of the spectrum and sensitive only to the shape.

Portions of the infrared spectra of five mixtures and the statistical correlation coefficients obtained are shown in Fig. 9. These calculations were made by taking the spectra and summing the point-by-point product of each pair of absorbance values as indicated in the preceding algorithm. Had we started from the table of quantitative parameters, these coefficients could have been obtained more directly from an algebraic expression derived from the above equation by integration.

The third method for qualitative identification involves writing a computer program which incorporates all of the empirical rules spectroscopists now use for interpretation. The computer can look for carbonyl bands and other indicators of functional groups and summarize the results of such a search for the analyst. A major advantage of such a program would be that the computer would never forget the rules that had been programmed, and new correlations could be added by the introduction of a few program statements.

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