

# ANALYSIS INSTRUMENTATION

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VOLUME 11

1973

# **ANALYSIS INSTRUMENTATION, Vol. 11**

**Proceedings of the  
19th ANNUAL ISA ANALYSIS INSTRUMENTATION SYMPOSIUM**

**April 24-26, 1973  
St. Louis, Missouri**

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Library of Congress Catalog Card No. 56-29277  
ISBN 87664-200-8

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## FOREWORD

This volume contains the proceedings of the 19th Annual Symposium of the Analysis Instrumentation Division (AID), of the Instrument Society of America. This symposium was held in St. Louis, April 24, 25 and 26, 1973, and was part of the First ISA Joint Spring Conference in cooperation with the Chemical and Petroleum Industries and Process Measurements and Control Divisions as well as the Education Committee. All of the papers for which manuscripts were submitted within the required deadline are included.

The basic charter of the Analysis Instrumentation Division is to provide a focal point for exchange and dissemination of knowledge and experience in all aspects of laboratory and process analytical instrumentation incorporating chemical, thermal, electronic, spectral and chromatographic principles. The annual symposia provide the primary platform but in addition, the division sponsors short courses and inter-society conferences and publishes monographs and tape cassettes, through the cooperation and facilities of the parent society.

The division officers and the parent society officers are listed on the acknowledgments page along with the symposium technical program committee and the host committee of the St. Louis Section.

Without the dedicated labor of the session developers and their authors, the symposium could not have been. These men are identified in the contents listing.

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## OPERATING PRINCIPLES OF A NEW COMPOSITION ANALYZER

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### ABSTRACT

A new composition analyzer, which employs novel optical techniques, has resulted from consideration of the requirements which must be met in modern process control applications. This analyzer may be described as a "composition transmitter", because it provides continuous concentration information about a single chemical species present in a sample taken from a multicomponent stream. Basic design considerations were reliability, dependability, specificity, accuracy, insensitivity to environmental conditions, and tolerance of sampling system deficiencies. The further requirement that in-service field maintenance be quick, simple, and easy to accomplish, without special or unusual tools or procedures, was strictly imposed.

A single-beam, multiple-wavelength infrared measuring scheme that makes use of an energy-transport type focused optical system is used. This provides high specificity and relative immunity to the effects of the deposits that will inevitably build up and "dirty" the optical surfaces in any realistic application. The use of sealed internal standards, for automatic zero and span recalibration, removes the otherwise constant need for external supplies of standards materials. Thus, instrument calibration can be checked by using certified standards only at infrequent intervals. Sophisticated and yet simple signal processing techniques are employed to assure reliable performance. The output is linear in concentration and is provided via the 4-20 ma. signal standard, or through other output options.

### INTRODUCTION

Instrumental control of processes in the chemical and petroleum industries has been employed for several decades. Over most of this period the information which formed the basis for control came from single-function sensors that measured temperature, pressure, or flow. This information was then generally used to actuate simple control mechanisms.<sup>(1)</sup> The realization that more complete process information could be used in more complex ways to achieve better control has led to an evolution of control strategies and the means of implementing them. Further, today's economic facts of life have intensified the need for instrumentation that can help to keep a process running and running properly. The difference between "on-spec" and "off-spec" is increasingly the difference between profit and loss.<sup>(2)</sup> There is also a widening realization that the key to optimum process performance is continuous analysis of product, and of selected feed and intermediate process streams.<sup>(3)</sup> Optimization of plant operations, as well as process performance, can be a result of the further understanding that instrumentation can improve plant safety;<sup>(4)</sup> especially when it becomes possible to directly measure process variables of interest for control and safety.<sup>(5)</sup>

Advances in sensors (and thus the quality of process information) in combination with advances in the means to use such information (whether through more advanced controllers or with computers) have combined<sup>(6)</sup> to define an era of control technology that places further demands upon the sources of process data. In particular,

"Superior numbers refer to similarly-numbered references at the end of this paper."

and in spite of exciting advances over the last decade, analyzers are still commonly regarded as the weakest link in control technology. An examination of the requirements of modern process control reveals why further advances in analyzer technology are not only desirable but imperative.

### REQUIREMENTS OF MODERN PROCESS CONTROL

There are several categories of considerations that, together, define whether a process analyzer can satisfy today's application demands:

1. In-service performance. How reliable is the operation of the analyzer? How specific is it in the performance of its defined function?
2. Data quality. Is the quality of the process information good enough for control? Can the user depend upon the information being an accurate reflection of current process conditions? (7)
3. Environmental tolerance. Will the analyzer continue to perform in the plant environment for long periods of time? Will short-term environmental fluctuations adversely affect the quality of data? Will the analyzer be forgiving of the sampling environment and tolerant of sampling system deficiencies? (3, 8, 9)
4. Maintainability. Is the design one which recognizes that analyzer failures can, and will, occur? Is repair by replacement possible and straightforward? (10) Does the design make it readily possible to field-calibrate? (11) Are the benefits of standardization recognized in the design? (12) Is it easy to determine whether the analyzer is working properly?

5. Adaptability. Can the analyzer be readily adapted to various applications by trained specialists? Or do problems of reactivity, stability, or purity impose limitations? (13) Can functional components be readily changed to accommodate the demands of a particular application?

All of the above considerations have direct impact upon the suitability of an analyzer for on-line application and must be recognized in its design. Yet, all of these considerations cannot be met simply through a "big, expensive, do-everything" design. The process analyzer which we describe was developed to satisfy these many considerations which arise from the realities of field applications.

### OPERATING PRINCIPLES

A two-wavelength, single-optical-path scheme, using narrow band interference filters for wavelength selection (out to 12  $\mu$ ), was chosen as the basis for this analyzer because it is tolerant of obscuration of optical surfaces, including sample cell windows. It is unlikely that the obscuring material would be opaque at one specific wavelength and transparent at another specific wavelength; because the beam obscuring material will be solid (or liquid), and it will most likely be opaque at both wavelengths. By using the ratio of intensities at the two different wavelengths as the basis for measurement, the analyzer is inherently tolerant of "crud" (obscuration) of the optical surfaces.

Several analyzer designs that employ two-wavelength measuring schemes have been described (14, 15, 16, 17, 18, 19) and a number of these use multilayer interference filters for wavelength selection. These filters are fixed in their passband characteristics, unlike dispersive elements such as prisms or diffraction gratings used in conjunction with slits, and the stability of their fixed characteristics is extremely good. (19) The wavelengths chosen for a particular application cannot be changed except by changing the optical filters. This means that "adjustment"



of these wavelengths cannot be made except by properly authorized personnel and then only by replacing a modular component as part of a predetermined change-over of the analyzer. The use of filters also means that the chief cause of wavelength instability in a dispersive system is not a factor; that is, mechanical stress due to ambient vibration, shock, thermal cycling or corrosive action.

An energy-transport type focused optical system is used in this analyzer design in order that the optical energy may be precisely and efficiently conveyed along the folded optical path which is employed. This is not a focused system in the conventional, "everyday" sense; that is, one in which a clear, crisp image of some object is formed at a specific point. Rather, the purpose of this system is to achieve certain desired spatial distributions of the optical energy at specific locations along the optical path.\* For example, the beam does not touch any portion of the sample-cell except the end-windows, and at the windows the beam divergence is small. As a result of this optics design all of the optical surfaces which can be "dirtied" are perpendicular to the beam path, or nearly so, which assures that the principal mode of beam energy-loss is simple obscuration.

The practical consequences of this type optical system are quite important in the realities of field use; (a) alignment of the sample-cell is not a critical matter and therefore it can be "snapped" into and out of mounting clips for easy servicing and, (b) no part of the sample-cell except the demountable end-windows requires cleaning. And, unlike most other optical analyzers which can operate in the infrared, this one does not require a sample-cell with a polished interior surface because the measuring beam does not contact the interior surface of the cell.

As shown in Figure 1, there are two other cells besides the sample-cell through which the optical beam may be directed. These two reference cells may be referred to as the "zero-cell" and the "span-cell"; they normally are sealed internal standards used for automatic recalibration of analyzer "zero" and "span". When the focused measuring beam is directed through the zero-cell, the ratio of the measuring and reference wavelength intensities is taken

as "zero" because the zero-cell does not contain any of the subject chemical species for which the analyzer was set-up. Likewise, when the measuring beam is directed through the span-cell, the ratio of measuring and reference wavelengths is taken as "span" or "full-scale" because the span-cell contains a concentration of the subject species which corresponds to the desired span of the analyzer.

Figure 2, which is a photograph taken of the analyzer with the cover of the explosion proof housing removed, shows one of the reference cells and the sample cell "snapped" into place. The heater housing which normally would surround these cells has been removed to expose the cell mounts. One end of the optical mechanism which directs the measuring beam through the desired cell can be seen in front of, and to the right of, the sample cell. The infrared source has also been removed to show the filter cell, which may be "snapped" into place between the source and the rest of the optical system to increase discrimination ratios for specific interfering chemical species. When the measuring beam is directed through the sample-cell, as it normally is except for brief recalibration periods, the intensity ratio then measured is used to compute the fractional concentration of the subject species. This fractional concentration signal is then passed to a linearization circuit which provides an output signal that is linear in concentration units between the zero and span end-points. The sources of drift, etc., which can affect the validity of the zero and span recalibration factors are both small and long-term. Hence it is necessary to direct the measuring beam to the reference cells and compute new zero and span calibration constants only every few moments. Therefore, the analyzer continuously measures the concentration of the subject species except during brief and well-spaced recalibration periods; during these periods the output signal is held at the last value measured, prior to recalibration, so that there is no bump due to the recalibration action. An internal timer sequences the analyzer through recalibration action frequently enough to accommodate even extreme changes in ambient conditions. The result is that the analyzer is effectively and continuously calibrated against the internal zero and span reference standards and thus provides on-stream information which is "current" better than 95% of the time. For the remaining fraction of the time, the output information is "out-of-date" by only the fraction of a minute spent in recalibration action.

\*In this usage "focusing" does not have the familiar, everyday meaning and is not a critical matter.

The consequences of employing internal reference standards are several: 1) zero and span calibrations are automatic and periodic; 2) flow of the process sample through the sample-cell is not interrupted because there is no need to switch the flow to calibration mixtures; 3) supplies of calibration mixtures are never required nor consumed; 4) there is no chance of an incorrect supply of calibration mixture being used to replace an exhausted supply; 5) certified external calibration mixtures may, however, be used to check analyzer performance as the user's own preference dictates; 6) there is no danger of the supply of a calibration mixture being exhausted at an awkward moment (for example, when no back-up is available).

An obvious limitation to this technique of using sealed internal standards is the stability of the standards. For subject species that are stable, the limitation is imposed by the effectiveness of the sealing of the reference-cells. The requirements posed here are no more stringent than today's practice achieves. For unstable subject species, the affected reference-cell may be readily changed at suitable intervals, (with automatic recalibration), or an imitative reference mixture may be used. A flowing reference may always be used as an alternative, if desired for any reason.

The electronic circuitry which comprises the control, signal processing, and computational functions is all solid-state and is designed so that there are a minimum number of inter-connections between component packages and a minimum number of connectors employed. All circuitry is protected from the hostile atmosphere in which the analyzer may operate by using several techniques; potting, shrouding, plating, etc. Because field reliability and maintainability are fundamental design requirements, premium grade electronic components are used and the number and types of components are restricted in the interests of standardization. Further, the electronics package is designed with a goal of "component-independence"; that is, individual electronic components can suffer substantial degradation of characteristics before performance of the analyzer is noticeably affected. (Ideally, we would like this to be so to the limit of actual component failure but in practice we can only approach this limit.)

One consequence of the nearly component-independent design, and the automatic recalibration scheme described above, is that the electronics package does not include a raft of "twiddle-pots". Maintenance is thus simplified to the level of repair-by-replacement<sup>(10)</sup> on a modular scale and the chances of inadvertent, unauthorized, or ill-advised misadjustment of the analyzer are greatly diminished.

## PERFORMANCE

The analyzer we describe is designed to perform well in a wide variety of control applications. To illustrate its performance characteristics we've chosen as an example the measurement of a stream component (n-butane) which may be measured in several multicomponent streams in a refinery. The particular characteristics shown are: 1) the large dynamic range; 2) the discrimination against interfering species; 3) the tolerance to obscuration of the optical path.

Figure 3 shows the basic internal response\*, with a fixed sample-cell length, for increasing concentrations of n-butane. The linearization scheme operates throughout this range and thus, for this particular cell length, a wide range of span calibrations could be chosen. Another way of looking at this is to say that the analyzer will operate over a very wide range of tangential sensitivity. For the region of the dotted line in Figure 3, a shorter cell should be chosen.

Figure 4 illustrates the specificity of measurement obtained with practical optical filters. In this case the apparent concentration of n-butane is plotted versus actual concentration of iso-butane. With the analyzer set-up for n-butane measurement, a mixture of iso-butane and dry nitrogen was flowed through the sample-cell at various iso-butane concentrations up to 100% iso-butane. The discrimination against iso-butane shown in this figure was obtained without the benefit of any iso-butane in the filter-cell and thus is the unaided discrimination provided by the optical filters. Results are also shown for Propane.

\*Prior to linearization.

Figure 5 shows the tolerance of the analyzer design to obscuration of the measuring-beam path. The data were taken by partially covering (obscuring) one end-window of the sample-cell with a piece of dead-black heavy paper. As the plot of measured concentration versus percentage obscuration shows, the principal effect of even very great obscuration is to increase the uncertainty of the measured value; that is, to increase the noise on the analyzer output. This is as expected, because with the two-beam-in-time (single optical path) scheme which we employ, the effect of beam obscuration is simply a worsening of the signal-to-noise ratio. A smaller effect of obscuration, which arises at high levels of obscuration, is a change in the apparent concentration of the subject species. It is a systematic effect that is apparently due to the geometry of the optical path. At 80% obscuration, the apparent change in concentration is less than 11% of span (full-scale).

## CONCLUSION

This new composition analyzer may be properly thought of as a "composition transmitter"<sup>(3)</sup> and is particularly suited for modern process control applications in which dependable, continuous composition information may be used to advantage.<sup>(20,21)</sup> This concept is further supported by the fact that the instrument is self-contained. Because it can provide a reliable and direct measure of a process composition variable it also has the potential of improving certain safety aspects<sup>(5)</sup> of control. This analyzer is qualitatively different from what has been available, particularly because it can be used for measurement of almost any hetero-nuclear gaseous species in the presence of interferors. Thus it is appropriate to re-examine previous decisions and/or attitudes concerning the use of composition information.

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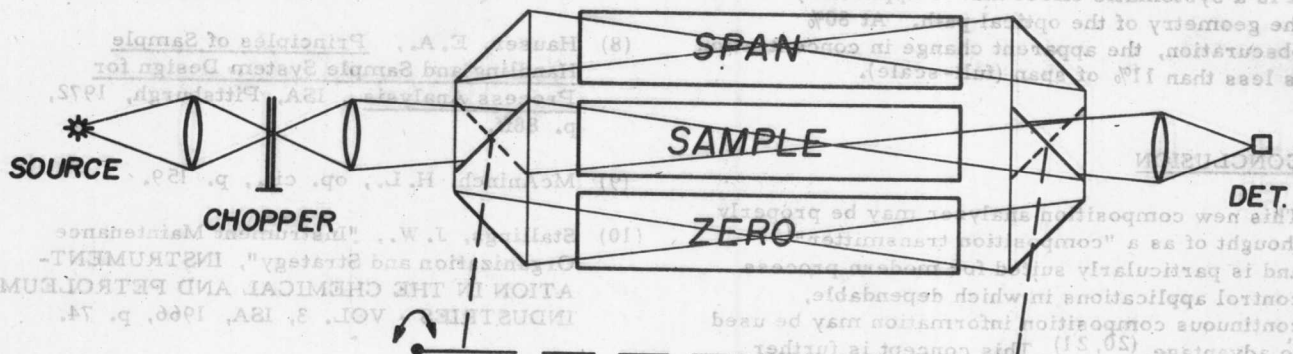
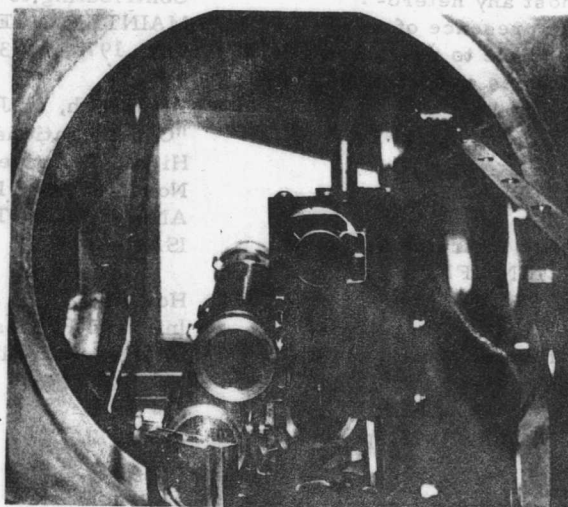


FIGURE 1. Functional Schematic of Cells.  
(SEE TEXT)



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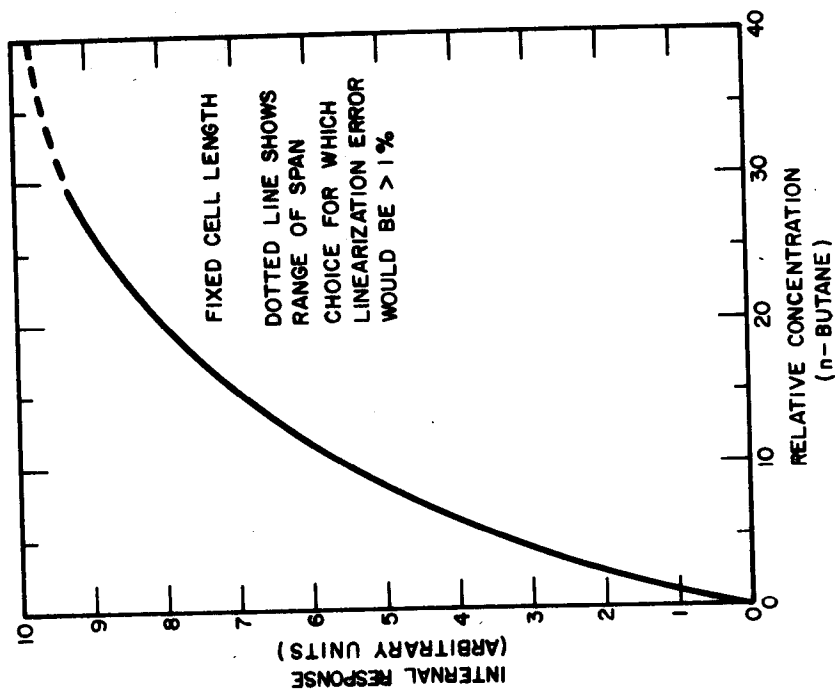


FIGURE 3. Internal Response Prior to Output Linearization.

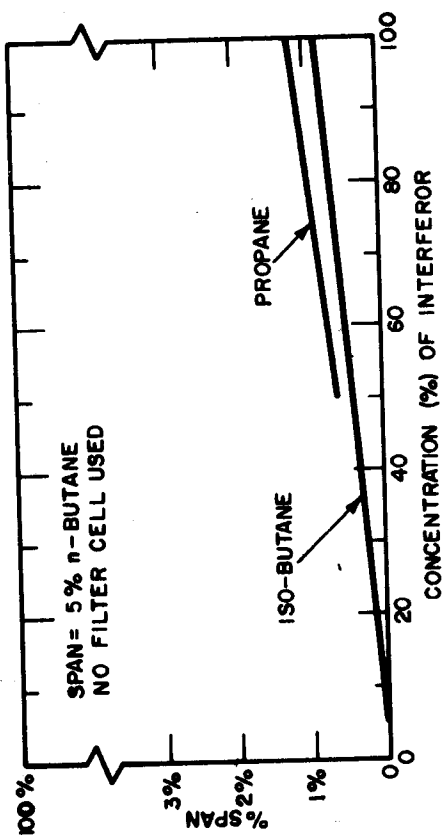


FIGURE 4. Analyzer Response to Interferors.

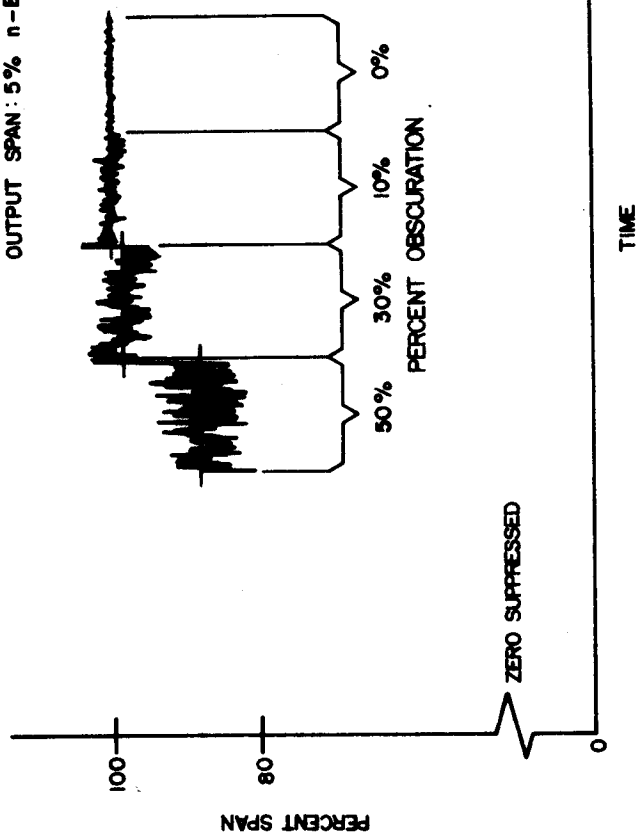


FIGURE 5. Effect of Sample-Cell Window Obscuration on Analyzer Output Signal.





## SPECTROCHEMISTRY WITH HTS INFRARED SPECTROMETERS

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### ABSTRACT

We describe the first commercially-available Hadamard-transform spectrometer (or "HTS"), the Spectral Imaging Model HTS-255-15 Analytical Infrared Spectrometer, and briefly detail the advantages of the technique for the analytical spectrochemist. We review the theory and history of HTS spectrometry, then present the design of this specific instrument - a 0.5 - meter,  $f/6.9$ , infrared system covering the 4000 to 666  $\text{cm}^{-1}$  spectral region at an average resolution of 3.5  $\text{cm}^{-1}$  which is designed for automatic operation by unskilled personnel in industrial environments. While time has precluded the inclusion of sample spectra in this manuscript, some typical infrared spectra obtained with this instrument will be presented and discussed at the Symposium.

### INTRODUCTION

We will discuss here a new technique and a new instrument. Specifically, we will discuss the Spectral Imaging Model HTS-255-15 Hadamard-Transform Analytical Infrared Spectrometer, (1) which is shown in Figure 1. This instrument offers a real revolution in spectrochemistry, as it provides orders of magnitude increase in spectral performance at no significant increase in either system complexity or cost. Specifically, the Model HTS-255-15 offers signal to noise (or sensitivity or observing time) gain factors from 200 to 50,000 while using a completely conventional dispersive spectral discrimination system. It therefore has the simplicity, reliability and economy of conventional scanning monochromator spectrometers, and yet is capable of fully automatic operation by unskilled personnel in industrial, field or "adverse" environments.

We will discuss the background of infrared spectrochemistry a bit, to look at the classical limiting factors and put the performance of these new instruments into context. We will then try to answer the question, "What is a Hadamard-transform spectrometer?", (1-3) and then go on to describe the system, its design, operation and performance. While typical infrared spectra

obtained with this instrument will be presented and discussed at the Symposium in St. Louis, the press of time has prevented these from being included in this manuscript.

### The Background of Infrared Spectrochemistry

The classic problem in spectrochemistry is the analysis of an unknown (that is, the identification of the chemical constituents of some object) by means of the structure present in its transmission or reflection spectra in the presence of interference from unwanted structure of the chemical being analyzed, spurious structure caused by various artifacts of the analysis system, and instrumental noise. This problem is particularly severe for infrared spectrochemistry, as infrared sources provide low flux levels and the low photon energy in the infrared precludes the use of photoelectric detectors. Specifically, infrared spectrochemistry has been historically plagued with noisy detectors which are themselves the limiting factor to system performance. Unfortunately for the spectrochemist, many molecular species of interest have their most characteristic structure in this region of the spectrum. The result has classically been that infrared spectrometry is, indeed, a major analytical tool, but one has had to put up with either noisy spectra or very long observation times, and one is continually facing a serious interpretation problem in the evaluation of noise and spurious spectral artifacts.

There have long been two solutions open to the instrument designer and the spectrochemist to at least partially overcome these limitations. The first, of course, is simply to increase the amount of light that the instrument handles, i.e., to increase its throughput (or "etendue") and thereby increase its sensitivity and decrease the amount of time required for a given measurement at a given signal-to-noise ratio (this has become known as the "Jacquinot advantage" (4)). The other possible design solution has been to make the instrument sensitive to all the wavelengths of a given spectral region simultaneously, rather than sequentially (as is done with a conventional scanning monochromator). This allows the instrument to recover the signal energy that would

Superior numbers refer to similarly-numbered references at the end of this paper.

otherwise have been blocked by the exit slit of the monochromator and wasted. This is particularly important in overcoming the limitations imposed by detector noise, and hence is particularly appropriate for use in the infrared, and has become known as the "multiplex" or " Fellgett advantage" (5)

These design approaches have been previously available to the spectrochemist only in the form of interferometric spectrometers: the so-called Fourier-transform spectrometers, employing scanning Michelson interferometer geometries. These Fourier-transform systems are elegant and provide superb performance in the right hands (the Connes in France, for instance, have recorded spectra on an interferometer with a total pathlength difference of over 1.5 meters which multiplexes over 1-1/2 million individual spectral elements). These systems, however, are interferometers, and therefore are comparatively complex and precise instruments, requiring very high fabrication and alignment accuracies and tending to be expensive and a bit on the fragile side for use in routine analysis in industrial environments.

The Hadamard-transform spectrometer which we are describing here has essentially the same performance as a Fourier-transform system - that is, it accepts essentially the same amount of light and it views all of the wavelengths in a spectra simultaneously. However, Hadamard-transform spectrometers use dispersive spectrometric technology in conjunction with binary optical logic in achieving these ends, and are therefore consistently less complex than Fourier-transform systems and of considerably lower cost and higher reliability. While the chemist who uses his infrared spectrometer but rarely will probably find both systems much too esoteric for even momentary consideration, we feel that the Hadamard-transform spectrometer offers revolutionary advantages for those spectrochemists needing more sensitivity or signal to noise in their spectra, or require shorter observation times than they can now obtain. HTS systems, additionally, do this at far less cost than Fourier-transform systems and are, in fact, cost-competitive with the higher quality scanning monochromators.

#### Hadamard-Transform Spectrometer

The theory of the Hadamard-transform spectrometer is well known (1-3) and will not be presented in detail here. However, since the technique is probably new to all but a handful of my readers, I think it appropriate to briefly answer the question, "What is a Hadamard-transform spectrometer?", before we proceed to a description of this specific instrument system; we will answer this question by referring to a logic diagram, Figure 2, first proposed by Peter Fellgett (6) in the context of Fourier-transform spectrometry and adapted by us (7) earlier for this purpose. The system we are describing here is represented by the cross-hatched region at left center marked HTS.

First, a Hadamard-transform spectrometer is a multiplex spectrometer: that is, it is sensitive

to all the wavelengths of a given spectral region simultaneously, rather than one at a time as is done with conventional scanning-monochromator spectrometers. Second, a Hadamard-transform spectrometer is a transform spectrometer: the output data signal is a mathematical transform of the input optical spectra. Here, we use one of a family of binary pseudo-noise transforms based on Hadamard matrices; hence, the name "Hadamard-transform spectrometers." This family of binary functions has all the properties necessary for encoding and modulating signals in optical multiplex systems, yet takes on only two values, 0 and 1, and hence are ideally suited for implementation by means of multislit grids and for decoding in a digital computer. Finally, the Hadamard-transform spectrometer is not an interferometric instrument, as it is best implemented by the use of multislit arrays in conjunction with conventional dispersive spectrometric optics. That is, it uses the grating or prism spectrometers familiar to us all in conjunction with binary coded multislit masks.

Now, one can well say, "This is all very well; we grant that the mathematicians have devised binary analogs to most of the familiar sine/cosine analog mathematical functions and that it would be desirable to use less complex optical arrangements than an interferometer. However, how in practice can one implement the scheme?" The answer to this is that the implementation is surprisingly straightforward and simple. One uses multislit coded masks, as mentioned above; that is, arrays of slits coded according to the appropriate mathematical function. These slit-arrays replace the exit slits (or the entrance slits or both) of an otherwise-conventional dispersive spectrometer. The total intensity passing the spectrometer for various positions of this slit-array is recorded and this information is then used by a digital computer to reconstruct the original spectrum.

To see how this operates, let us consider the simplest case, that of a spectrometer with a single entrance slit and a Hadamard-coded multislit array in lieu of the conventional exit slit. The light entering the spectrometer is dispersed by means of a grating or prism (which remains fixed), to form a polychromatic image of the entrance slit at the exit focal plane. This dispersed radiation is then collected on a single infrared detector for various positions of the mask. Let us assume that we have  $n$  spectral elements and that the coding mask therefore has  $n$  discrete slots (that is, locations on the mask which can be either opaque or transparent). If we now take  $n$  measurements (the same number of measurements we would normally take to define an  $n$  point spectrum), we have recorded a series of  $n$  weighted averages of the total light within the spectral region, where the weighting is different for each of the  $n$  different recordings. This is shown mathematically by Equations 1, below, where the coefficients  $a_{i,j}$  determine whether a slit is transparent or opaque for a given color at a given measurement, the independent variables  $x_j$  are the spectral power densities we wish to determine, and the  $I_i$  values on the right hand side is the sequence of total intensity measurements. What we have done

**this particular mask is the exit (spectral encoding) mask for the Model HTS-255-15 Analytical Infra-red Spectrometer.**

[illegible]

$$[a_{i,j}] = [S_{19}^T] = \begin{bmatrix} 0111100110110000101 \\ 1011110011011000010 \end{bmatrix} \quad (4)$$

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101100001010111001
110110000101011100
011011000010101110
001101100001010111
100110110000101011
110011011000010101
1110011011000010101
1111001101100001010
0111100110110000101
1011110011011000010
0101111001101100001
1010111100110110000
0101011110011011000
0010101111001101100
0001010111100110110
0000101011110011011
1000010101111001101
1100001010111100110
0110000101011110011

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0110000101011110011011000010101111001 (5)

The above argument pertaining to exit coding accounts for the HTS Spectrometer's multiplex property, that is, its ability to look at all the wavelengths of a given spectrum simultaneously. It turns out that one can also independently operate a similar mask at the entrance of the spectrometer to greatly increase its light grasp. (10) It then shares with the Fourier-transform spectrometers the "Jacquinot advantage". (4) The mathematics of this Multislit-Multiplex operation is extremely complex; we should think of it here as a "cascading" of the matrix algebra of the above argument to an additional stage. Fortunately, it is much less complex to do than to describe mathematically (particularly since one seldom wants to widen the entrance aperture beyond a few millimeters). The 15 slot cyclic Hadamard-encoding entrance mask used on the Model HTS-255-15 Spectrometer is shown in Figure 4. Additionally, if one chooses the correct code and mode of operation, it does not require either any additional observing time or any additional data points per spectrum to obtain the wider aperture.

The use of this second mask allows the additional possibility of spatially resolving the observed object. (11) The standard multislit-multiplex Hadamard system, such as our standard commercial instruments, have a one-dimensional imaging capability: one merely changes the data taking and data analyzing routines somewhat (with no hardware changes). This means that one can get independent spectra of one-dimensional "slices" across an object or higher-signal-to-noise-ratio spectra averaged over the whole object. We should also note that it is possible to get a full spatial/spectral image of an object, through the use of an appropriate two-dimensional coding mask at the entrance of the spectrometer. This is described in the technical literature, (11) but since it has no current spectrochemical