COMPUTERIZED SPECTROSCOPY

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OF all the recent advances in computer technology time-sharing appears to be the most meaningful for the laboratory analyst. Unlike the more widespread tasks of handling reams of essentially identical data—keeping tabs on people and products and money—the lab man's job is to make sense out of complex data. From a fuzzy signal he must extract an unambiguous percent concentration. So many factors interact to give rise to the signal that the effect of each must be isolated, evaluated and weighted before the reported percent concentration resembles actuality. Instead of the sprawling computer capable of spitting out huge amounts of similar data he needs a sophisticated device. Versatility, not volume, is the keyword. Versatility has meant expense and until the advent of time-sharing suitable computers were out of reach of all but a very few laboratories.

More powerful and dependable than last decade's "giant brains," today's computers sport the latest in hardware fashion, and at bargain prices. Integrated circuits have replaced solid state components which replaced vacuum tubes which were great inventions not so long ago. But among the really elite in computer circles is the "software" designer who writes languages in which mortals may converse with the brainchildren of our era, computers. The likes of him have assembled collections of instructions and methods of generating instructions for computers, programs and executive programs that control the paths of other programs within a computer to ever so sophisticatedly exploit its efficiency. And now time-sharing—the method of feeding one high-speed central processing unit from and to many low-speed input/output devices—brings it all to your nearest teletype machine.

The reality of time-sharing is, itself, a product of significant recent developments like new random-access memories
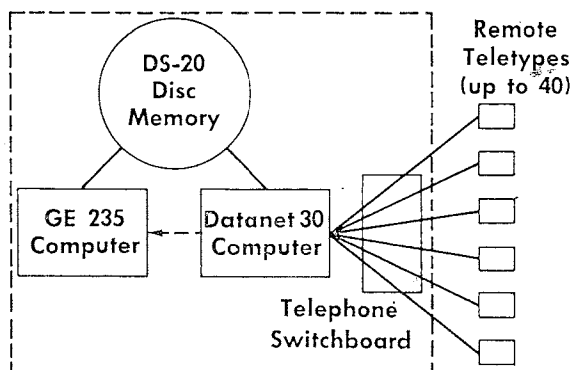
GE-265 TIME SHARING SYSTEM

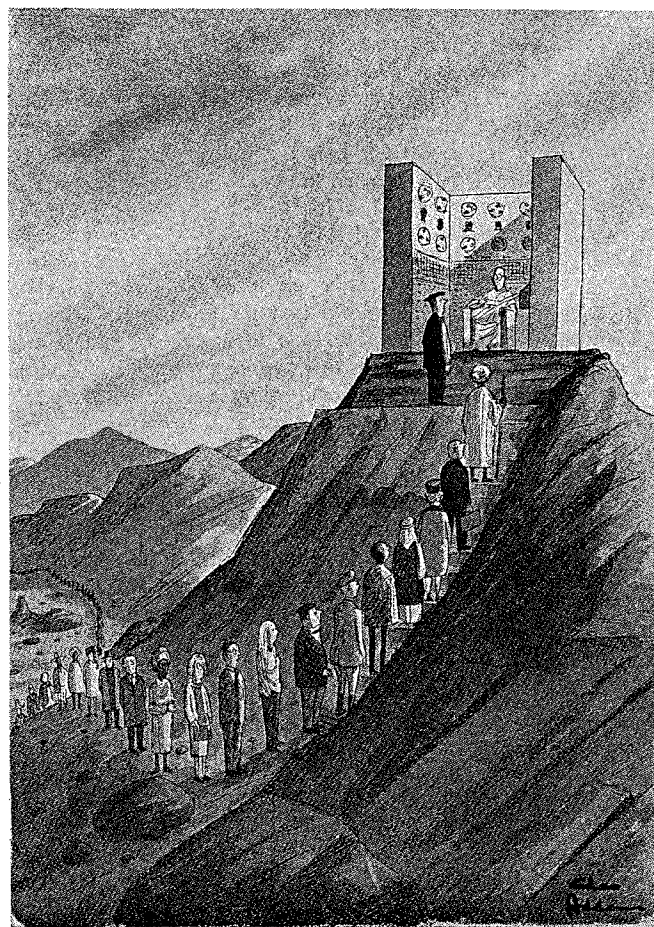Figure 1: Schematic diagram of the GE-265 time-sharing system.

Figure 2: Drawing by Chas. Addams; ©1967 The New Yorker Magazine, Inc.

on magnetic discs, drums, or cards. These serve as auxiliary memory devices to supplement the high-speed core memory, and have access times in the millisecond range, as compared with microsecond range for cores. While slow in comparison to core speed, they are much less expensive and have helped make large-scale time-sharing systems really practical. An example of a time-sharing computer is the GE-265 system shown schematically in Figure 1. The actual calculations are performed for this system by the GE-235 central processor which shares a large magnetic disc memory with the Datanet-30 communications computer. Datanet-30 contains the time-sharing software or executive program which handles all communications between the operator terminals and the main computer, stores temporary working copies of programs being entered, and decides the priority of each request and other system operations. At a teletype terminal (which can be lo-

cated in one's own office or laboratory) the system behaves as though it has no concurrent programs, even though forty other people may be working with it at the same time. The disc memory contains the system program library as well as each of the privately saved programs, all instantly on call. Every program for which a "RUN" command is given is accepted by the GE-235 central processor for an increment of 3, 6, or 12 seconds, depending upon the length of the calculation, and is then sidetracked to a queue on the disc memory while the programs of other subscribers are processed. Since most requirements are for only a fraction of a minute (usually from 5 to 30 seconds) of computer time the queue moves rapidly and as a rule everyone gets his printed results within a few minutes.

Other time-sharing systems with a hardware configuration similar to the GE-265 are the GE-600 system at Dartmouth College where the central processor is a large GE-625 computer with two Datanet-30s in control and the Telcomp system of Bolt, Beranek & Newman of Boston in which a small PDP-8 computer controls a PDP-7 central processor, with on-line auxiliary storage on magnetic cards. The direct man-machine dialogue, known as "real-time interaction" eliminates the requirement of all questions being prepared in advance. Unplanned questions, not foreseen in setting up the program, may be asked and answered. The framework of the problem may thus be altered while it is being solved.

Computers understand only electrical impulses coded in the binary system. The trouble in their early days was that they rarely did what they were told to do. Improvements in both hardware and software have completely changed the picture and the trouble now, according to Professor Kemeny of Dartmouth, is that they do exactly what you tell them to do, not what you meant to tell them to do [1]. He was referring to the exacting demands set by the languages in which programs for a digital computer must be written. Mastery of this language in fact has been a major barrier between the problem bearers and the computer. With the growth of computing centers, a hierarchy of programmers and specialists, elevated to a technological priesthood, interpret problems for the computer, which generally stands on some remote peak as in the Charles Addams drawing, Fig. 2.

While the time-sharing technique brings us direct communication with that remote computer, the language problem remains to block any really effective man-machine interaction. Realizing this, Professors Kemeny and Kurtz of Dartmouth College devised a language called BASIC (Beginner's All-purpose Symbolic Instruction Code) [2] for the time-sharing system used by Dartmouth students and faculty. It eliminates the unessential formalities that discourage conquest of FORTRAN,* but retains the essential algebraic structure of that language. This simplified code is taught to students at Dartmouth in one three-hour lecture, after which they are placed on their own at a teletype terminal with an instruction book. BASIC is now provided on the commercially available GE-265 time-sharing system [3] along with FORTRAN and ALGOL. It is not a toy but a complete scientific tool that any technically educated person can master in about a week of interacting with the computer over a teletype line. Professor Kemeny, who spent the war years at the computing section in Los Alamos where the various numerical calculations necessary for the design and construction of the first atomic bomb were carried out, estimates that a sophomore at Dartmouth could, starting from scratch, solve in one afternoon's time all of the problems that

kept the computing section at Los Alamos working overtime for a year and a half [1].

What the impact of this development on science and technology eventually will be is impossible to predict because we are now at the point where people are just beginning to realize what time-sharing is all about. The GE-265 system has been commercially available for only a little longer than a year but already has thousands of subscribers in more than twenty cities across the nation. The much less well-known Telcomp [4] service of Bolt, Beranek & Newman, whose software includes only the conversational JOSS language developed at Rand Corporation, also has more than a hundred subscribers and is growing rapidly. What such time-sharing services have to offer is essentially equivalent to a private, general-purpose computer at a monthly subscription rate that small or occasional users are well able to afford. Other, more specialized time-sharing services have also been proposed. Thus, Control Data Corp. has designed a scientific desk calculator [5] that may be connected to a remote computer over any telephone set by means of a special acoustic coupler. Its unique symbol keys define functions, integrate or differentiate a defined function between preset limits, obtain values of logs, sines, cosines, or exponentials, perform statistical analyses, etc. The processing of requests is performed by a Control Data 6000 series computer, which can service about 200 of these terminals by devoting approximately ten percent of its time to the task. While this system is not yet commercially available, a somewhat less sophisticated electronic desk calculator, the LOCI-2 of Wang Laboratories, has recently become popular as a replacement for once ubiquitous mechanical desk calculators. Smallest of the available computers it goes far beyond its predecessors in performance and instantaneously displays exponentials, natural logs, square roots, and squares of an argument entered on its keyboard. In addition, programs of up to forty steps on hand-punched cards can be accepted. As an example, one program card operates on a set of data (such as replicate analytical results) from the keyboard and almost immediately displays the corresponding mean, standard deviation, and coefficient of variation. Needless to say, such statistical calculations are among the most tedious in an analytical laboratory and have tempted many people to invest in even a large computer.

AS Table 1 indicates, computers have been applied to all phases of analytical spectroscopy and related fields. Most categories can be described as either repetitive calculations or occasional use of a computer to handle some particularly tedious or difficult calculation. The cost of computerizing must be weighed in each individual case against the advantages to be gained from faster, more accurate results and savings in man-hours, plant operations, equipment turnaround time, etc., that are made possible. Some types of calculations are entirely impossible without the aid of a computer, while others are discouragingly slow when performed humanually. Sometimes, it is possible that the cost of time saved by adding an on-line computer to analytical instrumentation is so valuable that even an elaborate computer-controlled installation built around, for example, a vacuum direct-reading spectrometer becomes an economical proposition. Such is the case with computerized direct-reader installations controlling production of steel made in basic oxygen furnaces. These giant furnaces produce heats of several hundred tons of steel in less than an hour, and even a minute saved on each heat will add up to several hundred thousand dollars in a year's time.

What is often overlooked in setting up a large computer-controlled installation is the fact that the cost of the software package may be a significant fraction of the total cost of computerizing an analytical operation. Even under ideal condi-

* The first successful computer language developed at IBM ten years ago.

TABLE 1: SOME RECENTLY REPORTED APPLICATIONS OF COMPUTER TECHNIQUES TO SPECTROSCOPY AND RELATED FIELDS

(a) **Emission Spectroscopy**

1. Emulsion calibration.
2. Conversion of percent transmittances to relative intesities and intensity ratios.
3. Fitting of analytical curves to standard readings, both photographic and photoelectric.
4. Automatic conversion of direct reader output signals to concentrations.
5. Calculation of concentrations using the variable internal standard technique and the inert atmosphere spark.
6. Background corrections.
7. Matrix corrections for interelement effect and line interferences.
8. Studies of arc profiles using the Abel inversion to obtain true radial intensity distributions.
9. Arc temperatures from relative line intensities.
10. Dispersion curves for spectrographs or spectrometers.
11. Statistical data evaluation for homogeneity studies of standards, etc.

(b) **Flame and Atomic Absorption**

1. Distribution of emission and/or absorbance in flames as a function of sample concentration, flow rate, interfering element concentration, etc.
2. Interelement effect studies.
3. Automatic conversion of atomic absorption detector output signals to concentrations.

(c) **Absorption Spectroscopy**

1. Smoothing of digitized absorption spectra by a least-squares smoothing procedure.
2. Correction of band shapes for slit width error.
3. Resolution of overlapping bands into individual components.
4. Correction of wavelength errors.
5. Conversion of wavelength to frequency scale and vice versa.
6. Conversion of transmittances to absorbencies and vice versa.
7. Correction for base line drift.
8. Peak search.
9. Addition and subtraction of spectra to determine components of mixtures or to synthesize the spectra of mixtures for comparison with unknown spectra.
10. Library search and peak matching.
11. Fourier inversion of interferometer scans in infrared interference spectroscopy.
12. Synthesis of theoretical spectra from band intensity and position correlation data for functional groups.

(d) **X-ray and Electron Probe**

1. Fitting working curves and calculating concentrations in X-ray fluorescence spectroscopy.
2. Interelement corrections in fluorescence spectroscopy.
3. Absorption and fluorescence corrections in electron probe microanalysis.
4. Calculation of electron diffusion within an electron microprobe sample.
5. File search for X-ray powder diffraction patterns.
6. Fourier analysis of single-crystal diffraction patterns.
7. Computer control of X-ray diffractometer to speed up data collection for single-crystal diffraction patterns.

(e) **NMR**

1. Digital addition of spectral scans to increase signal to noise ratio and bring weak signals out of the background.
2. Smoothing to eliminate random noise.
3. Peak enhancement.
4. Correction for instrumental drift.
5. Fourier inversion of free decay of NMR oscillations to obtain normal spectrum from pulse excitation.

(f) **Mass**

1. Correction for line widening due to focusing errors on a photographic plate.
2. Evaluation of complex spectra to determine empirical formulas.
3. Peak matching and library search.
4. Addition and subtraction of spectra to analyze mixtures.

(g) **Activation Analysis**

1. Photopeak searching of gamma-ray spectra.
2. Photopeak area calculations.
3. Upper-limit calculations.
4. Weighted least-squares spectrum analysis.
5. Peak resolving.

(h) **Gas Chromatography**

1. Determination of integrated peak areas from digitized GC signals.
2. Correction for unsymmetrical peak shapes.
3. Correction for base line drift.
4. Automatic fraction collection.
5. On-line production control analyses.
6. Peak matching and library search.

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tions, one manufacturer of computer-controlled direct readers estimates that it takes a minimum of eight weeks (6) of a programmer's time to set up the necessary analytical curves and other routines. If it should happen that any operations or requirements on the system are not well defined the programming costs will of course skyrocket. They will also rise or fall in direct proportion to the time it takes the analyst to communicate his knowledge about the problem to the programmer who must then define it for the computer.

Usually, programs written for different computers and for different analytical systems are not directly interchangeable. If they were, and if the language barrier did not exist, it would be possible, at least in principle, to select and assemble one's own software package without having to explain every detail to a programmer on whose understanding of the problem everything depends. An approach to providing such a universal software package for spectroscopy lies in developing a higher-order computer language whose set of instructions would be simple English sentences functionally descriptive of the operations that are to be performed on spectral data fed into the computer. Such a language is being developed under the name of SPECTRAN by A. Savitzky (7) of Perkin-Elmer in Norwalk, Connecticut and Norman Jones of the National Research Council in Canada. The superstructure of this language is "open-ended" which means that new instructions and functional units can be added to it at any time. Its functional units are actually in the form of FORTRAN IV subroutines and

thus can be performed on any large computer currently in production and on most existing large computers. Reflecting the current research interests of the originators of this language, the first set of instructions for SPECTRAN will be for various absorption spectroscopic routines (listed in Table 1c). Emission, x-ray fluorescence, electron probe microanalysis, and other analytical subroutines and instructions, however, can be added to it later. The complete language may eventually contain far more features than an individual laboratory might profitably use. In such a case, subsets of routines such as SPECTRAN-A for absorption, SPECTRAN-E for emission or SPECTRAN-X for x-ray spectroscopy may become important for laboratories with different problems and instrumentation.

IT is worth our while to look into a few of the applications listed in Table 1 and our bibliography in order to get some idea of specific achievements.

Sometimes, a great deal of sophistication is not required for a computer to be effective. Addition of digitally recorded spectra, probably the simplest operation on digitized absorption and NMR spectra, can increase the signal/noise ratio in a spectrum by summing the ordinate values at each position for which a value is recorded. If N scans are digitally added in this manner the signal amplitude will be N times the signal amplitude for an individual scan while the noise will have increased by a factor of only $N^{1/2}$, yielding a net gain of $N^{1/2}$ for the overall signal/noise ratio.

Once a spectrum is digitally recorded, various scale transformations are easy to apply to bring it into a "standard" form. These transformations include wavelength to frequency conversion as well as percent transmittance to absorbance conversion in the case of absorption spectra. Corrections for base line drift and wavelength errors can be added and distortion of band shapes caused by the finite width of the slit function can be allowed for. High-frequency noise that tends to blur band shapes and mask weak bands in an absorption spectrum can be eliminated by a "smoothing" technique. Typically, the procedure consists of taking seven adjacent digitized points (or some other odd number, depending upon the density of digitized points and the noise spectrum to be suppressed) and fitting a parabola to them by a least-squares procedure. The ordinate of the center of the fitted curve becomes the ordinate value for that point of the "smoothed" spectrum. The next and following ordinate values for the smoothed spectrum are obtained by dropping one point from the left end of the original data set, picking up one point from the right, and repeating the procedure. If, instead of a parabola, another function is fitted to these points by the smoothing procedure the result may not be smoothing at all and may, for example, be band sharpening. Theory [8] indicates that maximum band sharpening is obtained if the smoothing function chosen has the natural band shape for the spectrum. Band sharpening by this technique has been actually demonstrated for NMR spectra where band width does not vary as much as it does, for example, in infrared absorption spectra. Band sharpening, unfortunately, also increases the noise amplitude and thus is not useful for weak bands in the presence of high background noise. If noise is first suppressed, however, by digital addition of a number of spectral scans and then band sharpening technique is applied to the resultant spectrum it becomes a very valuable method of resolving partially overlapping bonds or enhancing weak bands whose positions may otherwise be difficult to define.

Digital addition of spectra is of course not restricted to summing of spectral scans of a single specimen. Complex infrared absorption spectra of different compounds (after they are brought into standard form) can be combined to simulate the spectra of mixtures of these compounds without actually running a series of spectra for the mixtures. Such simulated composite spectra can be compared to the spectra of the actual mixtures to determine band shifts and other interactions that may have taken place among the components. Conversely, one may subtract the spectrum of a known compound from that of a mixture whose other components may be unknown. Afterwards, an attempt can be made to identify the remaining structure not accounted for by the known compound and so on until positive identification of all components is made. Computers are also handy for predicting spectra of completely unknown compounds from band intensity and band shift correlation data. Comparison of such theoretical spectra with those of actual compounds provide confirmation for the assumed band position and intensity correlations deduced from empirical data. Other operations that may be performed on digitized absorption spectra include resolution of overlapping bands into their theoretical components and automatic peak search and matching of peak patterns to those already indexed in a library.

When spectral scans are added for the purpose of noise reduction the question of the optimum number of scans in a given time must be carefully considered. Although the number of subdivisions of the total time interval does not influence the results as long as the noise amplitude at all frequencies remains constant, this situation may only be approximately true. Possibly more important, the physics of the situation may relate the signal amplitude to the scan rate. Such is the situa-

tion, for example, in NMR spectroscopy where the signal amplitude is higher for faster scan rates [8] and an increase in the overall signal/noise ratio will result if the total time available is divided into many short scans instead of a few longer scans. The best signal/noise ratio in NMR spectroscopy is in fact obtained if the spectrum is excited by a very short pulse and the decay of the NMR oscillations is observed. The spectrum of freely decaying NMR oscillations is a superposition of all possible frequencies to which the system is capable of reponding and must be subjected to a Fourier inversion in order to extract the usual form of the NMR spectrum from it. It turns out that, for the same signal/noise ratio, the total time required to produce an NMR spectrum by the pulse excitation technique is only one tenth that required to produce the same result by normal scanning techniques.

Physically different, but mathematically similar is infrared interference spectroscopy [9] where the raw signal is the Fourier transform of the usual infrared spectrum, produced by linearly scanning one of the mirrors in a Michelson interferometer which serves as the dispersing element. Lacking the resolution of prism or grating instruments, interferometers are several orders of magnitude higher in sensitivity and can be set to scan the entire infrared spectrum in a period of one second or less. Short scans are of course high in noise but a number of them can be digitally added and then a Fourier inversion performed to obtain an acceptable infrared spectrum. Major band structures are nevertheless discernible even when individual one-second scans are subjected to a Fourier inversion. Results obtained by Low [10] at Rutgers University (now at NYU) indicate that many published infrared spectra may be in error because the compounds involved are unstable so the sample at the end of a normal fifteen or twenty minute scan was no longer the same compound that was inserted into the spectrometer.

Deceptively simple in principle, atomic absorption spectroscopy has seen some of the most sophisticated computer techniques applied to fundamental analytical information. Ramirez-Munoz [11] and associates at Beckman Instruments in Fullerton, California with a cathode ray display terminal for a time-shared computer have plotted three-dimensional correlations among such factors as analyte concentration, interfering element concentration, and absorbance as a function of flame height, etc. They developed a program with a least-squares curve fitting routine to obtain a relationship between two variables when a third one is held constant. Varying the third in steps, then, they obtain a curve for each value and view a three-dimensional projection of the distribution on the scope. Grid lines can be added to this projection and the distribution rotated, expanded or contracted upon command. To record a desirable view of this distribution, the instrument produces a hard copy in a few minutes. Dr. Ramirez-Munoz has estimated that on his particular project the availability of the computer terminal increased his efficiency in analyzing the complex correlations among the different variables involved by a factor of at least fourteen.

In the field of x-ray fluorescence, computers have been programmed to make corrections for interelement effects based on the method of Lucas-Tooth and Price and thereby reduce the number of individual standards required to analyze many complex high temperature alloys [12, 13].

In electron probe microanalysis computer techniques have been used for quantitative calculations incorporating absorption and fluorescence corrections, as well as for theoretical studies of electron diffusion and x-ray production within the specimen. Perhaps the most interesting application to quantitative microprobe data is that reported by Lipschin [14] of General Electric Research Laboratories in Schenectady. Tak-

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2000 DATA 3100,1.585,4,97
2010 DATA1,2.05,2.05,4.3,4.3,9.1,1.25,2.5,2.5,5.5,5.5,12.1,12.1,25.6,3.1
2020 DATA 6.4,6.4,15,15,32.3,32.3,56.6,14.3,32.3,32.3,63.7,63.7,87.3
2030 DATA 87.3,96.1,36.4,66.4,66.4,89.6,89.6,97.1,71.6,92.6,92.6,97.9
2040 DATA 1.7,3.7,3.7,8.1,8.1,17.9,17.9,38.4,4.1,9.3,9.3,22.5,22.5,46.3
2050 DATA 46.3,74.1,11,27,27,55.6,55.6,79.5,79.5,93.7,52.1,79.5
2060 DATA 79.5,95.3,85.1,96.5,12.9,32,32,61.1,61.1,84.3,84.3,95.9,36.5
2070 DATA 66.9,66.9,89.7,89.7,97.5,71.6,92.8,9.1,21.3,21.3,47.1,47.1
2080 DATA 76.5,76.5,92.5,26.4,53.8,53.8,81.7,81.7,95.5,57.3,86.5,86.5
2090 DATA 96.1,11.4,28.1,28.1,57.4,57.4,83.6,83.6,95.3,32.5,62.5
2100 DATA 62.5,87.1,67.1,89.8,89.8,97,0
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Figure 3: Typical set of input data for KAISER, a BASIC-language program for handling emulsion calibration data (23).

ing an in-house GE-265 time-sharing system he developed a set of programs interconnected by "chaining" in such a way that any type of analyses could be handled by supplying only a few key facts such as x-ray take-off angle, atomic numbers of elements analyzed and the accelerating potential used. Some handy data compilations which would not have been feasible without large digital computers are the recalculation and publication of corrected x-ray mass absorption coefficients by Heinrich (15) and of wavelengths of x-ray lines and absorption edges by Dewey (16).

IN the field of emission spectroscopy the best-known computer applications are probably the on-line type of concentrational computers (17) that major manufacturers have developed within the last few years. Computerized vacuum direct readers are marketed now by ARL, Baird-Atomic, Jarrell-Ash, as well as Hilger & Watts in England. The hardware these instruments incorporate includes such small computers as PDP-8, LGP-21, IBM 1130, and similar systems. The largest number of computer-controlled spectrometers have been installed in the steel industry, although they are also found in large-scale smelters of other metals such as aluminum and copper. A computer-controlled spectrometer installation, once fully operational, is capable of analyzing a sample for fifteen or twenty elements, applying all necessary background and interelement corrections, and typing a complete report within two or three minutes. Needless to say, the cost of such an on-line system can only be justified if high volume and/or fast response are essential to the production operation. So we find computer-controlled spectrometers largely restricted to primary metal production control and to spectrometric oil analysis programs, for which Baird-Atomic has designed a spectrometric engine oil analyzer. However, all other emission spectrochemical data can and have been analyzed by various computers from small analog (18) to large digital types. A large digital computer was programmed by Boumans (19) in the Netherlands to convert percent transmittances of lines to relative intensities and intensity ratios, based on the Kaiser transformation, and then fit working curves to his data and calculate concentrations. He also calibrated his emulsion on the computer by fitting a straight line to a Kaiser preliminary curve. Similar work was reported by Svoboda (20) of Czechoslovakia at the XIV Colloquium in Hungary in August 1967. While these functions were calculated in a batch-processing computer, in this country time sharing brings such calculations into the laboratory by means of remote terminal operation. The GE-265 time-sharing system has been used for some time by the National Bureau of Standards (21) as well as by Grumman (22) to perform spectrochemical calculations on an experimental basis. Margoshes and Raspberry of NBS have devised over a dozen BASIC-language programs covering emission, x-ray fluorescence and electron probe studies. Here at Grumman we have developed a set of emission spectrochemical programs, also written in BASIC, that cover emulsion calibration, construction of working curves from data on standards,

calculation of concentrations either by the normal internal standard method or the variable internal standard technique coupled with the inert atmosphere spark, etc. All of these programs accept raw data in the form of percent transmittance readings and convert them into relative intensities (or logs of relative intensities) by means of the Kaiser transformation. The proper value of the Kaiser transformation constant is determined by feeding calibration data of the two-step variety into the emulsion calibration program which we have named "KAISER" (23). Too voluminous for printing here, the program instructions are available upon request from the author. Figure 3 is a typical set of input data for KAISER. The first set of data numbers are the wavelength, step ratio of the sector used, and two percent transmittances, one low and one high, which specify at which points of the preliminary curve the slopes of the H and D and of the Baker-Sampson curves are to be determined. The rest of the data are just percent transmittance readings in pairs (strong step first), followed by zero at the end. The program is set up to keep reading in data until this zero shows up, at which point the reading-in of data is terminated, the number of pairs recorded, and the next task started. All percent transmittances read into the computer this way are converted to Baker-Sampson Δ values, where $\Delta = \log (1/T - 1)$, and a quadratic least-squares fit

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KAISER        10:48      07/31/67
EMULSION CALIBRATION IN 3100 ANGSTROM REGION

STEP RATIO = 1.585 LOG(STEP RATIO) = 0.2
NO. OF POINTS USED = 60 NO. REJECTED = 0
WEAK STEP PCT. T RANGE: 2.05 TO 97.9
GAMMA DET FOR PCT. T RANGE 4 TO 1.94
Q DETERM. FOR PCT. T RANGE 97 TO 88.13

EMULSION CALIBRATION CONSTANTS:

     Q = 3.19 C.V. = 1.4
 GAMMA = 1.62 C.V. = 3.4
GAMMA/Q = 0.506 (KAISER TRANS. CONST)
  A(0) = 0.505319 A(1) = 0.888789 A(2) =-1.49967 E-2

CALCULATED EMULSION CALIBRATION CURVE

STEP NUMBER   PERCENT T      DENSITY        DELTA         K-VALUE

   1            98           0.01          -1.69          -0.85
   2           91.64         0.04          -1.04          -0.51
   3           73.14         0.14          -0.44          -0.15
   4           43.37         0.36           0.12           0.24
   5           19.78         0.7            0.61           0.66
   6            8.35         1.08           1.04           1.06
   7            3.71         1.43           1.41           1.42
   8            1.82         1.74           1.73           1.74
   9            0.99         2              2              2

DISTRIBUTION OF WEAK STEP INPUT VALUES

NO. IN CLASS:   0     5    10    15
HI PCT T LIM   I----I----I----I----I
    99.4       1X
    97.8       1XXXXXXXXXXXX
    92.6       1XXXXXXXXXXXXX
    78         1XXXXXXXXXXX
    50         1XXXXXXXXXX
    22         1XXXXXXX
     7.4       1XXXXX
     2.2       1X

DO YOU WANT TRANSFORMED INPUT VALUES, YES(1) OR NO(0)? 0

OUT OF DATA IN 120

TIME:   7.30 SECS.
```

Figure 4: Output of KAISER obtained by inputting the data in Fig. 3.

of Δ (strong step) against Δ (weak step) is performed to obtain an analytic representation for the Baker-Sampson ("Seidel") preliminary curve. The coefficients defining this preliminary curve are given in the output in Figure 4 as A (0), A(1) and A(2), along with all the other information derived from the preliminary curve. This specifically includes the slopes of Δ and of the H and D curve, the Kaiser transformation constant gamma/Q and a table defining the characteristic curve proper. The values of the Kaiser transformation (K-VALUE column) in the output are computed with the transformation constant determined by the program, and afford a means of checking how linear this transformation actually is for the set of data used. The distribution of the input data into eight classes, evenly spaced on the Δ scale, printed out with X's in a bar graph, should be a guide in estimating the degree of reliability of the output of the program for this data. Although the distribution is not the same for different wavelengths or different emulsions, it nevertheless becomes a significant qualitative parameter after a number of sets of calibration data have been processed. If the analyst should want to look at his data in even more detail, he can do so by typing a "1" in response to the question at the end of the output in Figure 4 and get a printed list of his input data as well as the values of all the functions corresponding to each input. The choice is given because normally time is not taken to print out all this data if everything else looks all right. The program in its present form can accept up to 100 points, which is more than adequate to construct a well-defined preliminary curve.

It might be guessed that when percent transmittances are to be read into the computer the human typist is the weakest link and manual typing should be avoided in favor of automatically digitized and taped data. While this is not too serious with an emulsion calibration program like KAISER
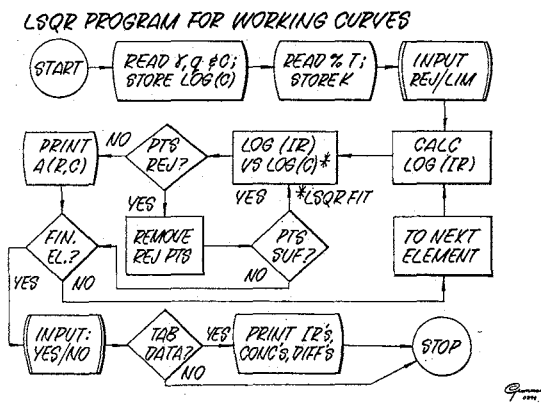
LSQR PROGRAM FOR WORKING CURVES

Figure 5: Simplified flow diagram of a BASIC-language program for fitting working curves by means of a least-squares procedure.
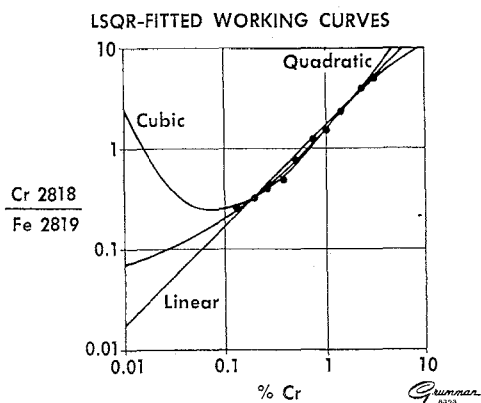
LSQR-FITTED WORKING CURVES

Figure 6: Different degrees of polynomial working curves fitted to the same set of data.

TABLE 2:
CONSTRAINTS ON LSQR-FITTED WORKING CURVES

- LSQR Fit is Applied to Log (IR) vs Log (C) Curve
- Highest Order Polynomial is Quadratic
- Resort to Linear Fit if <4 Pts are Given or Total Log (C) Range is <0.5
- If Quadratic Term is too Large or Goes Negative, Assume Non-Random Errors & Use Linear Fit

where the amount of data to be fed into the computer is modest, it is impractical to process any large volume of microphotometer data on the computer if they are not automatically taped when produced. Assuming that such digitized and taped data are available, the time-sharing computer can effectively and economically fit analytical curves to data from standards and analyze unknowns with coefficients that define the fitted analytical curves for each of the elements. Figure 5 is a simplified flow diagram of a program that fits analytical curves to standard readings by a least-squares procedure. Study of a large number of fitted working curves such as those in Fig. 6, suggested some restrictions on the curve fitting procedure (Table 2). Figure 7 is a typical output of this program. Only a few lines need be changed to calculate working curve coefficients with the variable internal standard technique, which in conjunction with the inert atmosphere spark, allows universal working curves to be established for a large number of alloys of only slightly similar matrices (24). To calculate the concentration of an unknown by this technique, the sum of all elements, including the internal standard element, is made to converge to something near 100% by an

```
LSQR-4    17:06    N2 WED 10/18/67

WORKING CURVE DATA--PLATE NO. 101.65

NO. OF STDS. = 11    GAMMA = 1.4    Q = 2.95

CONC. LIMITS AND PREC. MEASURES. STATE NO.OF SIGMA REJ.? 3

ELEM.  STDS. LOW LIM.  HI LIM.  COEF.VAR.        EXTRAPOL'N ERROR
1      11    .16       1.54     2.7              4.2
2      11    .16       1.54     4.8              7.6
3      11    .047      .96      12.6             18.5
4      11    .13       2.97     6.9              8.7
5      11    .19       4.98     9                11.4
6      11    .08       1.51     10.9             14.2
7      11    .024      .65      8.1              10.2


WORKING CURVE CONSTANTS. TYPE '1' AFTER QUESTION MARK.

ELEMENT      A[R,0]    A[R,1]    A[R,2]        ? 1

1001    DATA .820893 , 1.16809 , .183155
1002    DATA .31607 , 1.09669 , .166268
1003    DATA .551217 , 1.01577 , .173547
1004    DATA .217189 , 1.08309 , .186318
1005    DATA-6.93266 E-2    , .75514 , 3.77053 E-2
1006    DATA .238745 , .693473 , 0.
1007    DATA 1.29999 , 1.27061 , 8.21029 E-2'


DO YOU WANT CONC. VS. INT. RATIO DATA, YES[1] OR NO[0]? 0


TIME: 21 SECS.
```

Figure 7: Typical output of the least-squares program for fitting working curves. The working curve constants are outputted in a form that can be put on paper tape which becomes direct input to another program that calculates concentrations. Extrapolation error is given for a point one log cycle beyond the highest standard.

iteration procedure devised by the author (24) with another computer program whose flow diagram is Figure 8. The iteration to any aim concentration for the sum of elements goes very rapidly and is quite insensitive to starting values. Thus, three iterations only are required to reduce the residual concentration discrepancy in the sum to less than 0.01 percent.

In addition to these major programs the GE-265 has also been assigned several subsidiary tasks, such as the so-called C/IR-1, reproduced in its entirety in Fig. 9. It simply accepts the coefficients defining working curves that were obtained by the least-squares procedure and prints the concentrations and intensity ratios which establish the computed curve. The least-squares program also has an option providing printed out computed intensity ratios with which to check the fit produced by the computer by plotting the input values over the computed curve.

Other data the GE-265 has chalked up include calculation of the dispersion curve of a Czerny-Turner spectrograph (Spex 1800), tabulation of the solution of a differential equation occurring in the theory of spark discharges (25) and Abel inversion of arc profiles (26) to obtain true radial intensity distributions.
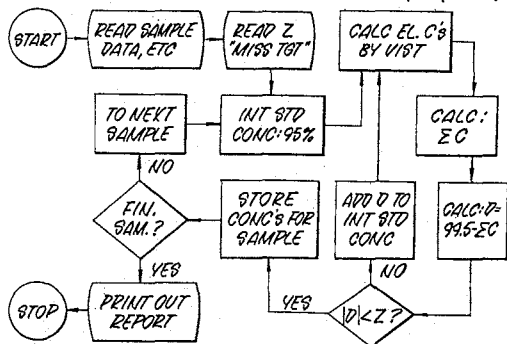

Figure 8: Simplified flow diagram of a BASIC-language program for calculating unknown concentration by means of the variable internal standard technique (V I S T).

```
C/IR-1    17:29   N2  WED  10/18/67

100 REM  PROGRAM BY A.ARRAK--GRUMMAN EXT 3072--10/18/67
110 READ P,LO,N,C1,C2
120 REM P=PLATE NO.;LO=NO. OF ELEM.;N=NO. OF STEPS PER CYCLE
130 REM C1=LOW CONC. LIMIT;C2=HIGH CONC. LIMIT
140 REM FEED IN 3 VALUES OF A(R,C) FOR EACH ELEMENT.
150 REM DATA STARTS AT LINE 500
160 FOR C=1 TO LO
170 FOR R=0 TO 2
180 READ A(R,C)
190 NEXT R
200 NEXT C
210 PRINT "CALCULATED WORKING CURVES--PLATE NO."P
220 PRINT
230 PRINT"CONCENTRATION LIMITS:"C1;"TO"C2
240 PRINT
250 FOR C=1 TO LO
260 PRINT"--------------------------------"
270 PRINT
280 PRINT "ELEMENT NO."C
290 PRINT
300 PRINT "CONCENTR.","INT. RATIO"
310 PRINT
320 FOR Z=LOG(C1)/LOG(10) TO LOG(C2)/LOG(10)+1/N, STEP 1/N
330 LET K=A(0,C)+A(1,C)*Z+A(2,C)*Z↑2
340 LET Y=2-INT(Z)
350 LET J=2-INT(K)
360 PRINT INT(10↑(Z+Y)+.5)/10↑Y,INT(10↑(K+J)+.5)/10↑J
370 NEXT Z
380 PRINT
390 NEXT C
9999 END
```

Figure 9: Complete list of small BASIC-language program. This program produces a table of pairs of concentration and intensity ratio values for plotting computed working curves defined by three coefficients that were originally obtained by the least-squares procedure from experimental data.

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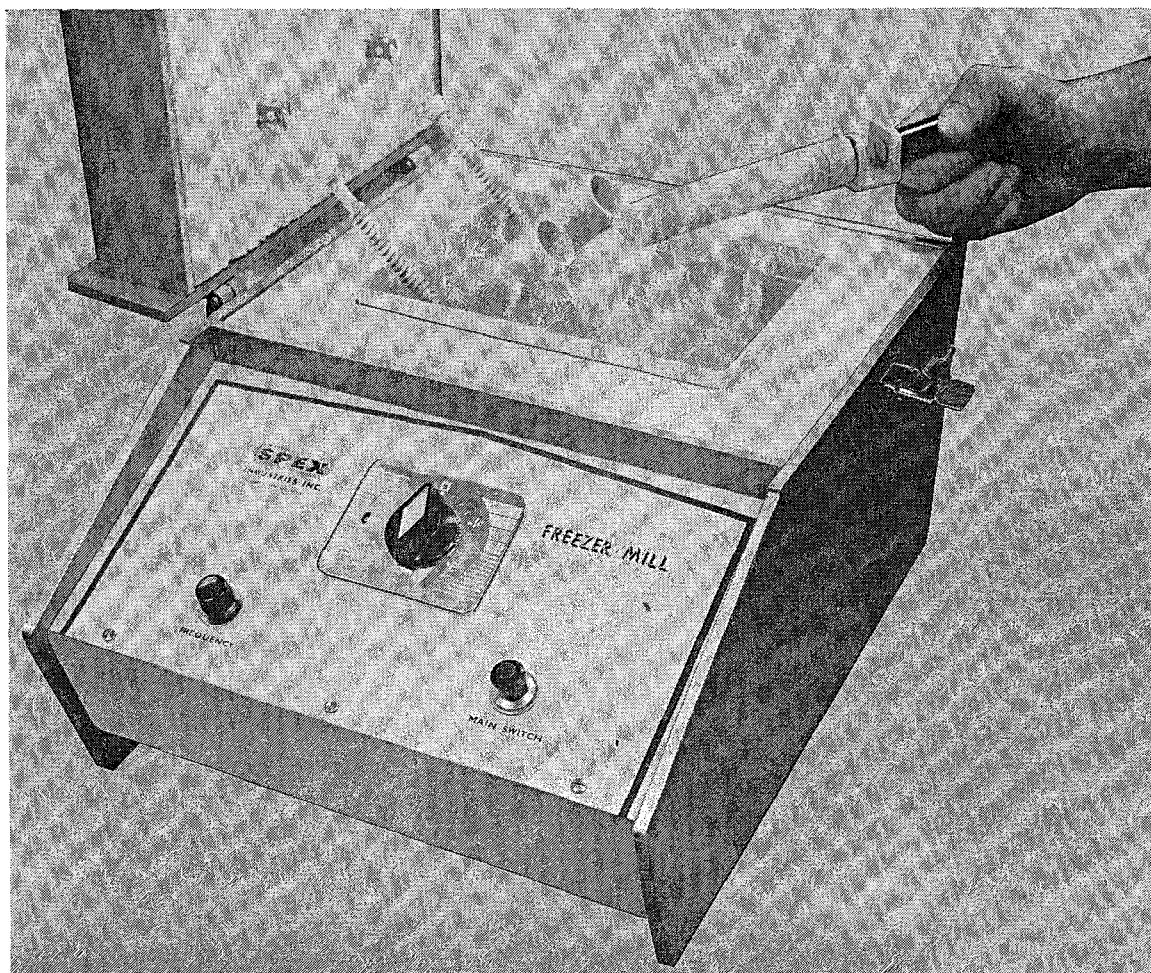
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