

ON-LINE COMPUTERS IN CLASSICAL CHEMICAL ANALYSIS†

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SUMMARY

Developments in digital electronics enable classical chemical analysis to regain some of the terrain lost to instrumental techniques. In chemical analysis, computerization can provide higher precision, higher speed and lower costs. The value of interactive systems in routine work is emphasized.

The exponential way in which digital hardware is developing has considerable impact on the concepts of laboratory instrumentation and automation. Automation in the laboratory not only relieves the experimenter from the tedious acquisition of data, lengthy calculations, drawing of graphs, etc., but in many cases enables higher precision in measurements and the optimization of procedures with regard to speed. In the field of classical chemical analysis, laboratory equipment is traditionally simple and relatively cheap, but the procedures are laborious and complex. This is in contrast to instrumental methods where the situation is somewhat reversed. Not surprisingly, computers were first applied to instrumental analysis, primarily to optimize the use of expensive equipment. Increasing labour costs and decreasing costs of computers and secondary memory now favour the introduction of computers in classical chemical analysis. Of course, the extent to which automation of an analytical method is justified depends strongly on the type of method and the goal of the analysis. In practice, it varies from situations in which a computer is used as a back-up peripheral for a specific analytical instrument to a fully computerized method incorporated into a laboratory computer network. It is as well to realize that the natural goal of instrument designers, i.e. completely automatic operation, often still produces some human tasks that are very unattractive.

Motives for computerization, technical possibilities and some human aspects are considered in the following sections.

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MOTIVES FOR LABORATORY COMPUTERIZATION

There is a variety of situations in which automation can resolve problems in the laboratory. The reasons for automation can be roughly divided into two groups: technical motives and reduction of human labour costs. The frequently-encountered technical problems that can be solved by automation are: (i) information is needed very quickly after the experiment or measurement is finished; (ii) an instrument has a high rate of data output; (iii) there is a complicated relationship between the information wanted and the quantities measured; (iv) the experiment has a complicated measurement protocol; (v) the experiment requires control information gained during the course of the experiment. Applications of on-line computers in the laboratory with emphasis on reduction of human labour mostly concern data acquisition, report generation and simple pre-programmed routine control actions.

COMPUTERIZATION OF UNIT OPERATIONS AND MEASUREMENTS IN CLASSICAL CHEMICAL ANALYSIS

Classical chemical analytical methods can be characterized as based on a chemical or electrochemical reaction. In this field, two fundamentally different categories can be recognized; (i) absolute stoichiometric methods in which all of the compound to be determined is converted, e.g., gravimetry, titrimetry and coulometry; and (ii) dynamic methods in which a reaction rate or a stationary state is correlated with the amount of the compound to be determined via a calibration procedure, e.g. polarography, voltammetry and potentiometry. Generally, the dynamic methods can be readily adapted for continuous operation. However, they are intrinsically less accurate than stoichiometric methods. Methods of both categories consist of a number of unit operations and measurements which differ widely in the ease with which they can be automated. A survey of the situation is given in Table 1, which is based on liquid samples. The handling of solid or gaseous samples is very much more difficult to automate. Other than current and voltage control, the unit operations can normally be controlled by reading and operating on/off switches. This task can easily be accomplished by any on-line computer, which offers much greater flexibility than discrete logic circuitry. Programming these functions at bit level can best be performed in assembly language.

Operations to position samples require mechanical or pneumatic gear that can be expensive, needs maintenance, and is prone to failure. They should be avoided as much as possible.

Traditionally, analog devices have been used to control current and voltage. Modern high-speed digital hardware enables on-line computers equipped with analog-to-digital converters (ADC) and digital-to-analog converters (DAC) to perform these tasks. Again the greater flexibility is an enormous advantage. Very complex voltage or current versus time patterns can be generated in this way. Use of the measured data in generating the control action can provide optimization with regard to speed and accuracy.

The computerization of a measurement generally boils down to the use of

TABLE 1

Ease of automation of unit operations and measurements in chemical analysis

Unit operation	Ease of automation	Measurement	Ease of automation
Sampling	—	Weight	+
Sample transfer	—	Volume	—
Reagent addition	+	Time	+
Stirring	+	Temperature	+
Heating	+	Light intensity	+
Distilling	—	Current	+
Cleaning	—	Voltage	+
Filtering	—		
Voltage control	+		
Current control	+		

a transducer that converts the quantity of interest to a voltage and digitalization of this voltage by an ADC. An exception is the measurement of time. Generally, on-line computers incorporate a high-precision oscillator, and counting its pulses provides a time base. It is noteworthy that many manufacturers of measuring equipment now provide digital outputs and inputs on their instruments, thus facilitating computer control of the instruments. Even standardization is appearing, as is testified by the acknowledgement of the IEEE 488 bus.

DATA TREATMENT AND TYPICAL MATHEMATICAL PROCEDURES

A large part of the software written for laboratory automation is specific to its application, and deals with complex calculations converting raw data to meaningful results with the use of algorithms based on the theory of the phenomenon studied with the computerized equipment. However, several processes recur in a variety of applications: signal averaging, digital filtering, direct digital control, and the display of results. This warrants some attention to these processes.

Signal averaging

For measurements which can be repeated, multiple data sets are collected in successive runs and finally averaged point by point. This improves the signal-to-noise ratio by a factor equal to the square root of the number of times the measurement is repeated. This technique is known as ensemble averaging.

Digital filtering

Noise of a specific frequency can be removed from signals by filtering. Analog filters have been used to this end but tend to be difficult and expen-

sive and cannot be easily adjusted to changing experimental conditions. A digital filter that is used very often is the one presented in the classic paper of Savitzky and Golay [1]

$$\bar{Y}_j = \left(\sum_{i=-m}^{i=m} C_i Y_{j+i} \right) / N$$

where Y represents the data samples, N is the number of data points ($N = 2m + 1$, called the span of the filter), \bar{Y} represents the filtered points, and C the filter coefficients, the values of which determine the operation of the filter.

Another type of filtering uses the Fast Fourier Transform [2]. It has been shown by Hayes et al. [3] that for electroanalytical data this method is somewhat faster than the Savitzky and Golay method, and the nature of the filter action can be interpreted more conveniently. The technique can also be used for interpolation of sampled electrochemical data [4].

Direct digital control

In titrimetric and electroanalytical methods there exist a number of control problems. Probably the best known are the control of the electrode potential (or sometimes current) in various electroanalytical methods, and the control of titrant addition (or generation for coulometric titrations) in set-point titrations. Much of the commercial gear available incorporates only some proportional control action for these processes. From industrial process control, it is known that much can be gained by the use of more elaborate controllers: i.e., with proportional, differential and integrating action. Eelderink et al. [5] have shown this for pH set-point coulometric titrations, which they were able to carry out in 12 s. These kinds of control actions can also be generated by software, and this is in fact common practice in industrial process control. Pomernacki and Harrar [6] showed the success of this approach for the control of electrode potential in controlled-potential electrolysis.

Display of results

The development of visual display units and plotters has opened up the way to almost perfect overviews of the results of automated measurements and calculations. Associated software (graphics) can be obtained commercially from the various computer manufacturers and software houses. Though a rather specialized field, this is of great importance as it can often be the determining factor in the success of a computerized method. The interactive use of graphics is very efficient in dealing with complex data as it combines the outstanding abilities of man and machine.

Although the need for visual inspection of the data, even for routine work with a well-tested method, has been recognized [7], the use of graphics is still not widespread in computerized titrimetric and electroanalytical methods. This is probably a result of the still relatively high cost of display hardware

and software. Developments in this area on the personal computer market show the use of cheap video graphic or alphanumeric displays. Skov et al. [8] chose this approach for a 256×192 -point graphic display for analytical applications.

Typical mathematical procedures

The possibilities offered by computers in the field of complex calculations have led to better use of data. On the one hand, there is a tendency to use all available data to obtain statistically improved results. On the other hand, work is being done to minimize measurements while simultaneously improving their accuracy in order to cut down analysis times [9]. Both approaches require rather complex calculations which are only feasible when done by computer.

In attempts to use all available data to extract information, two fundamentally different categories of methods can be distinguished. The first category includes the multiparametric curve-fitting methods; these methods require a theoretical equation relating the measurement variables to a number of parameters that describe the experiment. Starting with initial estimates, the parameters are adjusted in the calculations until the theoretically calculated values provide a best fit to the experimental results according to a least-squares criterion. The general curve-fitting program written by Meites and Meites [10] has been used in numerous applications of titrimetry and electroanalysis, e.g. in the evaluation of weak base titrations [11] and in the processing of overlapping polarographic curves [12]. The general program can be easily adapted to new problems by inserting the equation relating the experimental data to the parameters required. Not so easy to modify but much faster in execution are the multiparametric curve-fitting programs based on the mathematics given by Wentworth [13]. Recent applications can be found in titrimetry [14, 15] and polarography [16, 17].

In addition to the multiparametric curve-fitting methods, the first category includes methods which use linearization of potentiometric titration plots to obtain equivalence volumes [18–21]. Modified Gran functions play an important part in these linearization procedures.

In the second category, a statistical rather than a physico-chemical model is used to correlate the data measured and the information wanted. Early applications, mainly based on the Linear Learning Machine of Nilsson [22], were introduced in mass and infrared spectrometry by Kowalski, Jurs and Isenhour [23, 24]. The first application of these pattern recognition methods in classical analysis was reported by Sybrandt and Perone [25]; this concerned the deconvolution of severely overlapping peaks obtained by polarography at a hanging mercury drop electrode. The applications remained restricted to qualitative results until Wold et al. [26] recently extended their SIMCA method [27] to quantitative work, and Bos and Jasink developed systems for the quantitative evaluation of data from anodic stripping voltammetry [28] and potentiometric acid–base titrations [29].

AUTOMATED ANALYTICAL METHODS AND TECHNICAL STAFF

In the development of automated analytical methods, the tendency to allocate as many functions as possible to the equipment often leads to a residual set of unpleasant tasks for the analytical technician. Especially in classical chemical analysis, there is a fair chance that he will be left with sample preparations and book-keeping. Moreover, loss of control over the analysis can sometimes be frustrating, especially in cases where there is no interaction during the course of the analysis. A third cause of problems is equipment that hurries the operator.

In order to ensure smooth operation of an analytical laboratory and the wellbeing of the technical staff, attention should be paid not only to the design of automated equipment but also to the design of meaningful jobs for its users. Rijnsdorp [30] gives a number of rules for the allocation of functions between "man" and "machine" to create meaningful jobs that encompass a variety of tasks that exercise the operators' skills. He stresses the importance of close cooperation between those responsible for the technical subsystem (the technical engineers), those responsible for the social subsystem (the social engineers) and the (future) users of the technical subsystems.

CONCLUSIONS

It is clear that the computerization of classical chemical analysis is only at its beginning. The trend is certainly towards decentralized use of computing power by means of the application of microcomputers. Except perhaps for a few exotic electroanalytical techniques, the requirements with regard to the speed and the amount of memory of computers for classical analytical methods are rather modest. Hardware costs will therefore present no major problem. Much attention should be paid to software development and the design of methods that can be operated in continuous-flow systems in order to ensure the continuing use of classical analytical methods in an economic way. The great diversity of methods in this field points to multi-purpose laboratory equipment with flexible software that allows for interactive optimization of analytical procedures. However, there will remain a need for specialized equipment, especially for monitors in industrial processes and environmental control. Naturally the demands with regard to the computer part of such equipment are different, the emphasis being on reliability and speed of operation. Integration of analytical and process control operations will certainly lead to improved operation of chemical processes with less waste products.

No doubt some of the newer analog signal-processing devices will be important building blocks in this field. Worth mentioning are the tapped analog delay line, the potentialities of which have been described by Horlick [31], and the so-called analog microcomputer, a LSI combination of a fast ADC, a simple microprocessor, some EPROM and RAM memory, and a fast DAC.

As for the software, the availability of computer power (16-bit micro) in the laboratory will allow sophisticated data-processing methods. A very promising technique is the Kalman filter [32], the use of which enables real-time digital optimization of analytical information. Also pattern recognition types of data processing should find increased application, especially in cases where the relation between the information wanted and the data measured is complex. It is important to note that although the learning methods require lengthy calculations in training, the final recognition calculations are simple and very fast.

Finally it should be stressed that real achievement in the automation of classical chemical analysis will depend on integration of knowledge from analytical chemistry, electronics, and computer science. University courses in analytical chemistry, traditionally of a multidisciplinary character, are best suited to accomplish this integration.

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