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A new seagoing digitizing system for logging and processing AutoAnalyzer peaks using magnetic tape recorder and an off-line computer

by

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Abstract

A system of reasonable cost for the digital processing of AutoAnalyzer output is described. Retransmitting potentiometers are attached to the pen-drive mechanism of each AutoAnalyzer chart recorder. The 0 to 15 V output derived therefrom is digitized at 5 s intervals and recorded on magnetic tape. Upon completion of an analytical run this record and an identification tape are processed by off-line computer.

Introduction

Continuous-flow analysis, using instrumentation such as the AutoAnalyzer II is used widely in chemical oceanography, particularly for nutrient analysis. Large numbers of samples can be analyzed simultaneously for many chemical constituents with good precision and accuracy. Ordinarily the output of an AutoAnalyzer is obtained in analogue form as a series of peaks on a chart; that can be related to the concentration of the analyzed constituent. To handle the large volume of data generated by a multi-channel AutoAnalyzer during the course of an eight-hour run (240 peaks/channel at 30 samples/hour), automated logging and processing methods are desirable. Goulden and De Mayo (1971) and Caisey and Riordin (1973) have developed digital systems which rely on a paper-tape record and off-line processing by computer. These systems while inexpensive require the use of peak-holding meters, which

must be phased to allow peak heights to be read before the next peak appears. The system described here records the digitized value of the AutoAnalyzer output every five seconds. The complete record on magnetic tape is then processed by an off-line computer upon completion of the run. Computer programs are used to detect the peak heights, baseline drift, and blanks, and to calibrate. The concentrations of individual components are computed and stored on magnetic tape for further use.

Instruments and Methods

The system consists of a three-channel Technicon AutoAnalyzer II equipped for the analysis of silicate, phosphate, and nitrate in sea water. A Technicon Industrial Sampler capable of holding 100 samples is used at a rate of 30 samples per hour and a 1:1 ratio of sample to wash solution. A typical analytical run consists of the following sequence in the sampler: two blanks; a beginning set of nine calibration standards divided into low, medium, and high groups of three each; alternating sets containing two blanks plus ten unknowns; a finishing set of nine calibration standards, identical to those run at the beginning; and two final blank samples. The blanks contain the same low-blank solution used to make up the calibration standards (usually synthetic sea water).

We have found that, in order to maintain well defined and reproducible peaks with deep valleys between them, it is necessary to ensure that a bubble of air is entrained between sample and wash and vice versa. To do this: (1) a large industrial sampler is used, which switches more slowly from sample tubes to wash solution than the small Technicon sampler; (2) three individual probes are used, one for each method rather than a single probe; (3) plastic collars are placed just above the tip of each individual probe to prevent the solution from draining down the outside surface of the probe and entering the tip, where it would inhibit the aspiration of an adequate bubble of air between sample and wash.

The AutoAnalyzer II colorimeters produce a logarithmic signal proportional to the concentration of the chemical species present in the colorimeter cell. This signal is used to drive the pen of a chart recorder. To obtain the

signal for digitization we have followed the method of Goulden and Demay (1971) and use a retransmitting potentiometer attached to the shaft of each pen-drive mechanism of the chart recorders. A voltage of between 0 and 15 V is provided and any high frequency noise associated with the colorimeters is filtered out. The voltage across these retransmitting potentiometers is fed to individual channels of a Techal DS-869 digitizer capable of logging voltages from 16 independent sources with 0.1% accuracy. The sweep rate used is 5 s and the digitized voltages are recorded on a Kennedy 1600 HFC incremental recorder. The tape record for an 8 hr run thus contains, typically, some 6000 digitized voltages per channel. Programs to handle these tape records have been written for the Bedford Institute of Oceanography's Control Data 3150 computer. These programs have been adapted to the Hewlett-Packard 2100 minicomputers used on the ships.

Processing Program

The processing program reads, from cards or paper tape, information describing the run. The information includes the number of samples in the run, the number of constituents, the constituent assigned to each channel, the concentrations of the standards, and the number of voltage samplings per chemical sample. Also included are the identifiers for each peak in the run, that is whether it is a blank, calibration standard, or sea-water unknown.

Tape processing is then initiated. A record corresponding to one 5-s sweep is read and the signal voltages for each channel are decoded.

Until the signal voltage exceeds a preset threshold value, the program discards the reading and reads the next record.

The program then reads N records, where N is the number of voltage samplings per chemical sample. When the samplings corresponding to a complete peak have been read and stored, the maximum voltage in the set is stored as a resolved peak height (if the sample is identified as a calibration or an unknown), or the minimum is stored as a baseline value (if the sample is identified as a blank). This process is continued until all the peak-heights have been obtained. The program continuously checks phasing and resets the counting of succeeding N-point voltage-samplings on the previously selected

maximum. The expected position of the maximum in the interval depends on the sample to wash ratio.

Using the blank samples to determine a baseline, the program subtracts a local baseline voltage from each peak in the run. The calibration standards, of which there are three low, three intermediate, and three high concentration standards placed at the start and end of the run, are used to determine the coefficients for a linear regression of concentration against peak height.

The concentration of each sample is then derived from its peak height using the coefficients, and a correction is made to the concentration of each sample based on the nutrient content of the artificial sea water used for running the standards and wash.

The complete set of results for all parameters is then printed in tabular form, along with the identification information for each sample.

Discussion

The hardware configuration we have chosen is not unique. However, high-quality components are needed. The magnetic tape recorder must be compatible with the computer tape drives. The cost of the digitizing equipment is about one-quarter of the cost of six channels of an AutoAnalyzer II system.

This data logging and processing system is in its simplest state at present. Its utility depends on the production of well-behaved AutoAnalyzer peaks. It is not difficult to obtain such peaks if close attention is paid to Auto-Analyzer operational details, such as tube cleanliness and air-bubble formation, as described earlier. Those few peaks that may not form properly but contain a spike just at a digitizing point can be visually corrected; provision is made in the computer program for this. While more sophisticated subprograms can be included to allow for nonstandard peak-shapes, this has not yet proven necessary for the methods we have tried. To extend the system, for use with colorimeters of the AutoAnalyzer I type, it will be necessary to include only the calculation of logarithmic unit from percent transmittance, provided well-behaved peaks are obtained; if not, as is more usual with the AutoAnalyzer I, a more elaborate curve-fitting program will be required to obtain the peak-heights. Peak to peak interference can be corrected (as described by Thiers, Kirsch and Cole, 1966).

This logging and processing system has been used successfully both ashore and at sea, although we have not yet produced a data report for a full-scale cruise. Processing time on the 3150 and 2100 computers is five minutes or less per three-parameter run of 150 sample determinations. This system should prove useful to a variety of users who either do not need or do not want the expense of a system with on-line computing.

References

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