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AN INTEGRATOR FOR LOW ABSORBANCE SAMPLES IN ATOMIC ABSORPTION
SPECTROSCOPY¹

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¹ These studies were supported by Contract AT (04-1) GEN-12 between the Atomic Energy Commission and the University of California. The authors are indebted to T. Hartsock and R. M. Haug for technical assistance.

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Since the rediscovery by Walsh (1) in 1955, atomic absorption spectroscopy has become a very important technique for chemical analyses. More than 60 elements are determined routinely by using this technique (2). The sensitivity and the detection limits of these elements under specified analytical conditions have been published (2,3,4,5). The limiting sensitivity that is usually reported represents the concentration of a metal that will produce 1 per cent absorption. The detection limit is defined generally as the concentration in water solution that gives a signal twice the size of background variability (6). The background variability is the intrinsic instrumental fluctuation. Thus, by definition, an elemental detection limit may be interpreted as a form of signal-to-noise ratio. From an analytical point of view, the important quantity is the minimum concentration of metal that can be measured with useful precision. It is common knowledge that the precision and accuracy of sample absorption measurements become increasingly unsatisfactory as the detection limit is approached. This condition prevails for measurements made at less than 5 per cent sample

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1. From the Laboratory of Nuclear Medicine and Radiation Biology, University of California, Los Angeles, California 90024. These studies were supported by Contract AT (04-1) GEN-12 between the Atomic Energy Commission and the University of California. The authors are indebted to T. Hartsock and R. M. Haug for technical assistance.
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absorption unless stable scale expansion methods can be employed (7).

A large percentage of the analytical work done in this laboratory entails analyses of low absorbance samples. Consequently, in order to improve the precision and accuracy of measurements, an integration readout system was incorporated into our spectrophotometer system. By integrating the output signal from the spectrophotometer for a given period of time, the net charge consisting of information signal and noise can be accumulated. In this process, if the noise is random and the information signal is unidirectional, the information signal-to-noise ratio is improved because the noise component, at least to some extent, cancels itself out and thus, accumulates at a relatively slower rate. There are expensive, sophisticated systems that can do this efficiently, but for our purposes, the relatively inexpensive analog integration system was used. The system was that of Harrison and Berry (7) with several modifications. The analog integrator as presented by Harrison and Berry (7) was unstable with our spectrophotometer system when the input signal was small. This instability was traced to the time delay relay that was specified by Harrison and Berry (7). The relay caused baseline drift as its temperature increased after being energized. This is to be expected since the manufacturers' specification was 5 per cent tolerance of the time delay. This paper presents the modified version that showed greater stability in the range of low input signal. The use and performance of the modified version of the integrator is presented.

EXPERIMENTAL

Spectrophotometer

A Perkin-Elmer Model 303 atomic absorption spectrophotometer equipped

with Model 403 burner mount (Part No. 303-0410) was used to produce the signal for integration. The spectrophotometer was equipped also with an automatic recorder readout accessory (Model 303-0103), which produced an output signal proportional to the absorption of the sample and prepared it for presentation to a 10-millivolt potentiometric recorder (Perkin Elmer Model 165). The recorder readout accessory had provision for selecting absorption scale expansions of 1, 3, 10, 30 and 100 X. Any portion of the scale could be expanded. Since scale expansions increase the noise, the recorder readout accessory was provided also with filter circuits, which provided any of 5 damping times between 0.5 second to 2 minutes. The filter circuits sharply reduced the increased noise levels present at high scale expansions, but did not eliminate them. Thus, there was a practical limit of scale expansion, which varied with the element to be determined.

Integrator

The integrator that was put together at this laboratory was inserted in-line in the above spectrophotometer system between the recorder readout accessory and the recorder. The circuit diagram of it is shown in figure 1.

A two conductor shielded cable feeds the signal voltage from the recorder readout accessory to the input (buffer) amplifier (Analog Devices, Inc. Model 183 K). The feedback current to the selected integrating capacitor (1 μ Fd, 5 μ Fd or 10 μ Fd) on the second amplifier (Analog Devices, Inc., Model 230J) produces an output voltage which is impressed across

a voltage divider, the variable portion of which is a 10-turn miniature potentiometer (Helipot, 7240 Series). This controls the percentage of the output voltage applied to the recorder. Depending on the input signal magnitude, the output voltage range can be increased by a factor of 5 by shorting out the 40 K resistor with switch S5. Switch S3 provides a selection of 3 integrating capacitors listed above or the amplifier circuit which bypasses the integrating circuit. The integrating periods are initiated by throwing switch S2 to the integrating mode. This removes the shorting bypass from the integrating capacitor and applies a 115 V activating voltage to the time delay synchronous motor, which controls switch S6. This unit is equivalent to a model 78, Eagle reset timer. This timer has a repeatability of $\pm 1.5\%$, an adjustable time cycle of 0-60 seconds and a reset time of one second. The switch in this timer unit, which was originally a SPDT switch, was replaced with DPDT micro switch (Micro Switch No. DT-2R-A7). At the end of the timing cycle, a neon light goes on to indicate the end of the integration period and the readout trace on the recorder holds at the peak. Then, when switch S2 is thrown to the standby mode the integration capacitor is shorted and the readout trace on the recorder returns to zero (baseline). Also, the neon light goes out and the timer resets to the starting position.

Switch S4 has 3 positions. One position is used when balancing the buffer amplifier. The second is used when balancing the integration amplifier. These amplifiers are balanced with the use of the null meter while switch S3 is in the amplifier position. When the necessary because of the input

signal strength, the sensitivity of the null meter may be changed with the 50K potentiometer (Ohmite, 2W), which is not a front panel control. The third position of switch S4 is the operating position, which is used after the amplifiers have been balanced. The amplifiers are powered by a ± 15 V 4 ma. power supply (Analog Devices, Inc., Model 904). Balance controls are 10-turn miniature potentiometers (Helipots). Hermetically sealed, low leakage capacitors (Southern Electronics) were used for all integration time constants. The resistors used were low noise.

The preceding paragraph gives the components and the general operation of the integrator itself. In actual practice, the balancing of the integrator amplifiers was done by the use of both the integrator null meter and the recorder. The integrator null meter was used for coarse adjustment only. For fine adjustment, switch S2 was thrown to the integrating mode and the amplifier balance control was adjusted until the trace on the recorder chart showed no drift.

After the integrator amplifiers have been balanced, the chart baseline for sample analysis was set by adjusting the absorption range control of the recorder readout accessory until the trace on the recorder chart showed no drift. This was done with the water (other solvents) aspirating in the flaming burner and the integrator set for operation, i.e, switches S2 and S4 in the integrating and the operating modes and switch S3 at the selected integrating capacitor. In order to obtain easier control, the original 1 K potentiometer on the recorder readout accessory was changed to a two section, single turn 800 ohm potentiometer (Helipot, 5610 series) in the conjunction with a 200 ohm, 10-turn miniature potentiometer (Helipot, 7240

series). The former was used for coarse adjustment and the latter for the fine.

Procedure

Cesium was selected for testing the performance of the spectrophotometer with and without the use of the integrator. Cesium was selected firstly because it occurred in very low concentrations in the plant, soil and other materials that were of interest to us. Secondly, Cs required the use of vapor discharge lamps, because a hollow cathode lamp for it was not commercially available. The use of vapor discharge lamps exposed the integrator to a more rigorous test than using a hollow cathode lamp, because in our experience with the lamps of other alkali metals (K, Na, Rb), discharge lamps always were noisier than the hollow cathode lamps. Additionally, Cs has its sensitive resonance lines in the near infrared spectral region where the monochromator efficiency and the detector sensitivity are at the lowest. This, of course, would give poorer signal-to-noise ratio. Aqueous solutions of Cs (as nitrate) at the 0.5 $\mu\text{g/ml}$ concentration level was used throughout. The spectral line used for the analyses was 8521 $\text{\AA}$. The spectrophotometer operational parameters were always kept the same in comparing the results with and without the use of the integrator. The three-slot Belling burner head with air-acetylene flame was used. The solution aspiration rate was 5.2 ml./min.

RESULTS AND DISCUSSION

Figure 2 shows the recorder traces of the absorption from 0.5 $\mu\text{g/ml}$ cesium with and without the use of the integrator. In chart 1, 0.5 $\mu\text{g/ml}$.

cesium is seen to absorb about 1 per cent when the scale expansion (S.E.) of 1X and a noise suppression (N.S.) setting of 2 were used. The letter "A" represents the beginning of the sample aspiration period and "B" indicates the end. In chart 2, the scale expansion was set at 3X at the same noise suppression setting (N.S. 2). It is evident that the trace looks considerably noisier. By changing the noise suppression to a setting of 3, the noise was greatly reduced (Chart 3). This procedure of alternate change of the scale expansion and the noise suppression is continued through scale expansion of 30 X and noise suppression setting of 5. Scale expansion of 100X was beyond the capacity of the chart paper. The traces obviously became noisier as the scale expansion was increased. Thus, it was necessary to increase the noise suppression also. By the use of sufficiently high noise suppression setting most of the noise is eliminated. The peak and the baseline on the traces become easier to establish, but a certain amount of uncertainty involved in establishing these is not eliminated. Furthermore, high noise suppression, particularly setting 5, is very rarely used in our work, because of limited samples. The minimum recommended sample aspiration time when using noise suppression setting of 4 and 5 is 40 and 120 seconds, respectively. These disadvantages are made minimal by the use of the integrator.

Chart 8 shows the trace using scale expansion of 3X and noise suppression setting of 3 on the recorder readout accessory and the 1 μ Fd capacitor with a gain setting (G.) of 0.5 X 1 on the integrator. The

minimum recommended sample aspiration time for noise suppression setting of 3 is 15 seconds. The letters "C" and "D" indicate the beginning and the end of the integration period, which was set at 45 seconds for all our work. The operating parameters shown gave the most stable baseline with the 1 μ Fd capacitor; therefore, the trace shown was the best that could be obtained by using this capacitor. Charts 10 and 13 give the traces with 5 μ Fd and 10 μ Fd capacitors, respectively, keeping all other parameters the same. It is evident that the peak height decreased as the size of the capacitor was increased, making the absorption measurement less sensitive. These capacitors, however, could be used if the gain is increased. Charts 11 and 14 show the increase of peak heights caused by increasing the gain setting to 0.5 X 5. This gain could not be used with the 1 μ Fd capacitor, since it caused severe baseline drift (Chart 9). Another way to increase the sensitivity is by changing the scale expansion on the recorder readout accessory. Changing the scale expansion to 10X, while keeping the other parameters constant (Compare charts 14 and 15.) gave good workable trace using the 10 μ Fd capacitor. In fact, this combination of operational parameters (Chart 15) showed higher peak than the best that could be obtained with the 1 μ Fd capacitor (Chart 8). The scale expansion of 10X with the gain of 0.5 x 5 could not be used with the 5 μ Fd capacitor because of the baseline drift (Chart 12). It was necessary to reduce the gain to obtain a good baseline with the 5 μ Fd capacitor. From these results, it is evident that several workable operational parameter combinations can be used. With the 1 μ Fd capacitor, the minimum input

voltage to the integrator to obtain stable baseline was 0.5 mv. In general, because of its high sensitivity, the 1 μ Fd capacitor has been found to be difficult to use. Most of our sample analyses have been done with the use of the 5 μ Fd capacitor. In any case, the use of the integrator has improved the instrument sensitivity and the operator readability of the recorder traces of low absorbance samples.

SUMMARY

An analog integrator for low absorbance samples in atomic absorption spectroscopy is described. Its performance is demonstrated by the use of aqueous solution of cesium at the concentration level of 0.5 μ g./ml.

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FIG. 1 Circuit diagram of the integrator

MAJOR PARTS

- A Timer Motor
- B Power Supply-Analog Devices 904
- C Amplifier-Analog Devices 183K
- D Amplifier-Analog Devices 230J

SWITCHES

- S1 Power
- S2 Integrate-Standby
- S3 Time Constant-Amplifier
- S4 Balance-Operate
- S5 Integrator Gain
- S6 Time Delay

FIG. 2 Recorder traces of the absorption of 0.5 $\mu\text{g./ml.}$ cesium.

WITHOUT INTEGRATOR

WITH INTEGRATOR