

# Gas-Sampling Technique for Arsenic Determination by Atomic Absorption Spectrophotometry

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IN CONVENTIONAL atomic absorption spectrophotometry a solution of the sample is introduced into the flame as an aerosol by means of a nebulizer. However, commercial nebulizers are only about 5% efficient in forming fine droplets suitable for atomization by the flame (1). Furthermore, a solution aspirated at a usual rate of 3–5 ml/min for about 10 sec produces a concentration signal extending over the length of aspiration. Theoretically, if the element were introduced into the flame rapidly—e.g., 1 second—with no loss, a high narrow signal should result and the detection limit should improve.

Several devices aimed at improving the efficiency of atomic absorption sampling have been described in the literature. One scheme, developed by Brandenberger and Bader (2) was used to determine nanogram amounts of mercury. In their technique, mercury in solution was deposited on a copper wire and placed in the arm of a specially constructed cell with quartz windows. An electrical potential applied across the wire volatilized the mercury instantaneously. The mercury vapors were then swept through the cell with air and the atomic absorption signal was recorded as a function of time.

The above "flameless" technique cannot be used to determine arsenic because of the high temperature required to maintain arsenic in its vapor state. Arsenic often needs to be determined in trace amounts, and an improvement in the present detection limit of about 0.5 ppm would be desirable. This can be achieved if arsine is generated from the sample, collected in a cold trap such as liquid nitrogen, and then passed into the burner of an atomic absorption spectrophotometer, with the signal recorded *vs.* time.

## EXPERIMENTAL

All measurements were made on a Perkin-Elmer Model 303 atomic absorption spectrophotometer with windows removed to allow more light to reach the detector. The flame was air-acetylene with a three-slot Belling burner head. The signals were recorded on a Texas Instruments Servo-Riter 10-mV recorder as a function of time. The 1937-Å resonance line of an arsenic hollow cathode lamp was used.

A liquid nitrogen trap for arsine was prepared by bending a piece of glass tubing (550 × 8 mm o.d.) into a U-shape and 90 degrees outward near each end. The U-tube was filled with glass beads and rubber tubing was connected to each end. A thin needle of such an outside diameter as to fit snugly into the capillary of the aspirator was cemented to one end.

The U-tube was immersed in liquid nitrogen in a Dewar flask. A conventional arsine generator (3) fitted with a  $\text{CaCl}_2$  drying tube was used. After the sample (which contained as little as 0.5  $\mu\text{g}$  of arsenic) and the reagents were added, the generator was quickly connected to the U-tube. The set-up is illustrated in Figure 1.

When all of arsenic was converted to arsine (30 min) the generator was disconnected and the trap was closed with pinch

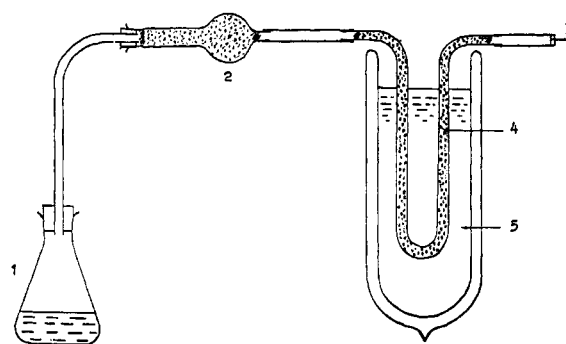


Figure 1. Arsine generator and liquid nitrogen trap

1. Arsine generator
2. Calcium chloride
3. Needle
4. Glass beads
5. Liquid nitrogen

clamps. The U-tube was removed from the liquid nitrogen and allowed to come to room temperature. Nitrogen at a flow of about 50 ml/minute was connected to the U-tube and the needle on the tube was inserted into the capillary of the aspirator of the atomic absorption spectrophotometer. Arsine was swept into the mixing chamber when the two pinch clamps were simultaneously removed.

## RESULTS AND DISCUSSION

The response varies with the number of arsenic atoms present (Figure 2). Preliminary results indicate that the detection limit is 0.04  $\mu\text{g}$  of arsenic. Peak heights were used to obtain absorbance values. A plot of absorbance *vs.*  $\mu\text{g}$  of arsenic indicates a Beer's law type of plot.

Two major requirements in this technique are that arsine be swept into the burner at a constant rate for a given analysis and that the electronic response of the instrument be rapid

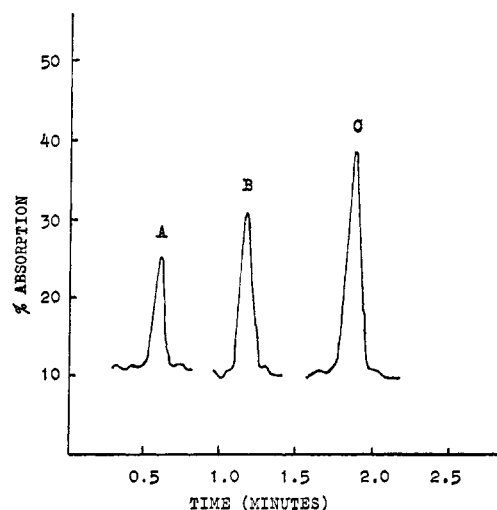


Figure 2. Signals produced by (A) 0.5  $\mu\text{g}$ , (B) 1.0  $\mu\text{g}$ , and (C) 1.5  $\mu\text{g}$  of arsenic

- (1) H. L. Kahn, Jr., *J. Chem. Ed.*, **43**, A7 (1966).
- (2) H. Brandenberger and H. Bader, *Helv. Chim. Acta.*, **50**, 1409 (1967).
- (3) "Official Methods of Analysis," 10th ed., Association of Official Agricultural Chemists, Washington, D. C., 1965, Section 24.005.

enough to detect the arsenic vapors passing through the flame. The optimum sweep rate can be found by experiment.

Admittedly, air-acetylene is not the flame of choice for the arsenic determination. A cooler, less absorbing flame (in the far ultraviolet) such as hydrogen-argon-entrained air (4) would be preferable. The latter flame is being used in further work.

The main advantage of the gas-sampling technique is its suitability for trace analysis. The element is isolated from the matrix and the total quantity is used to produce a sharp, absolute signal. In addition, interferences often associated with

solutions, such as the solids effect, and light scattering as well as chemical interferences are virtually eliminated.

Although the technique is described for the analysis of arsenic, it can readily be extended to other elements. Any element amenable to atomic absorption that can be converted to a gaseous or a volatile compound can be analyzed this way. Possible examples include silicon tetrafluoride, boron trifluoride, nickel carbonyl, and the hydrides of antimony and bismuth.

#### ACKNOWLEDGMENT

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(4) H. L. Kahn and J. E. Schallis, *Atomic Absorption Newsletter*, 7 (1), 5 (1968).

## Motor-Speed Control for Rotating Disk Electrode Systems

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USE OF FORCED-FLOW techniques permits the kinetics of chemical processes to be studied under steady-state conditions as a function of the rate of mass transport of reaction constituents to or from the reaction zone. For investigations of electrochemical reactions at solid electrodes, the rotating-disk electrode (RDE) system has proved to be of particular utility because the normal flux of a given species at the electrode surface is directly proportional to the square root of the angular velocity,  $\omega$ , of the disk (1, 2). To obtain accurate values of the mass transport and kinetic parameters which characterize the reaction rate, the rotational speed must be closely controlled (to within ca. 1%). Study of the relative degree of control of the overall reaction rate by kinetics and mass transport requires that the diffusion boundary layer thickness ( $\propto \omega^{-1/2}$ ) be variable by a factor of ten or more.

This communication describes the design of a simple motor-speed control for RDE systems which has been employed successfully in this laboratory for several years. The disk rotational speed can be varied continuously from 30 to 20,000 rpm without interchange of gears or pulleys. This range is generally adequate for most electrochemical investigations because near these limits, deviations from theoretical laminar-flow behavior occur, due to natural convective mixing at the one extreme and cavitation or turbulence at the other.

**Speed-Control Circuit.** A block diagram of the control circuit is given in Figure 1. The basic component of the system is a commercially available modular speed-control unit (Advanced Development Corp., Gardena, Calif., Model 10615-3) which employs two silicon-controlled rectifiers in a full-wave connection. The feedback voltage from a dc tachometer generator (TG) coupled to the motor shaft, either directly or *via* a belt-and-pulley arrangement, is compared with an internal reference voltage by a differential amplifier. (A tachometer generator such as Model No. SA-757A-2, with 7 V/1000 rpm output, manufactured by Servo-Tek Products Co., Hawthorne, N. J., is satisfactory. The nominal

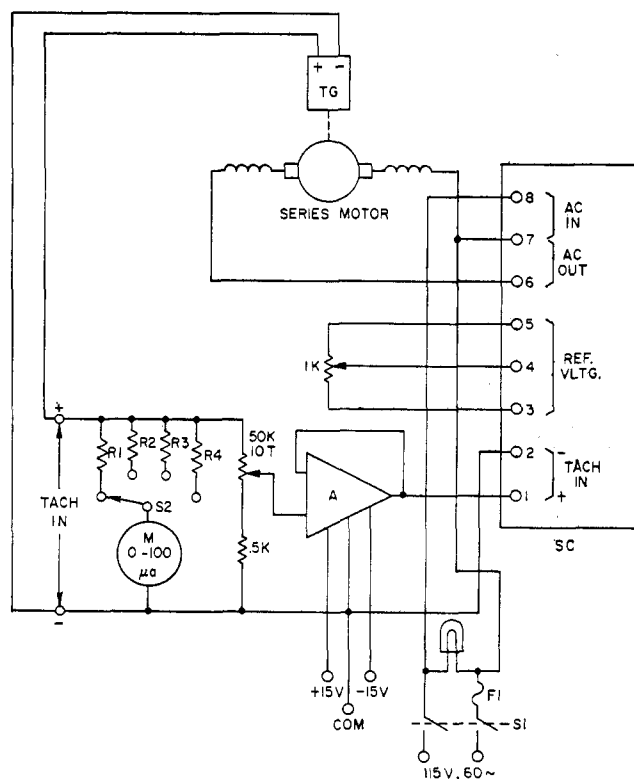


Figure 1. Motor-speed control for rotating-disk electrode systems

- A. Philbrick/Nexus Research P75AU (or equivalent) operational amplifier
- TG. Servo-Tek SA-757A-2 tachometer generator
- SC. Advanced Development Corp. 10615-3 control unit
- R1-R4. Series resistors, selected to give calibrated meter readings in rpm

maximum speed of this unit is 12,000 rpm. It may be safely employed at higher speeds with decreased service life and increased output voltage nonlinearity. Neither effect is of concern in the present application.) The output signal from this amplifier controls the firing angle of the SCR's in such a

- (1) V. G. Levich, "Physicochemical Hydrodynamics," Prentice-Hall Inc., Englewood Cliffs, N. J., 1962.
- (2) A. C. Riddiford, "Advances in Electrochemistry and Electrochemical Engineering," Vol. 4, P. Delahay, Ed., Interscience Publishers, New York, N. Y., p 47.