

## A 6800-MICROPROCESSOR-BASED POTENTIOMETRIC STRIPPING ANALYZER

Victoria A. Vicente and Florenda S. Valera  
*Department of Chemistry, University of the Philippines  
Diliman, Quezon City, Philippines*

### ABSTRACT

An inexpensive prototype potentiometric stripping analyzer (PSA), with options for oxidative or reductive stripping modes, was built from low-cost operational amplifier integrated circuits. The electrodeposition and stripping stages are controlled by electromagnetic relays, which are activated by a Motorola 6800-microprocessor available in the Heathkit Model EI-3400 microcomputer learning system. An interface circuit was constructed on protoboards in order to facilitate circuit modifications. It utilizes peripheral interface adapters, which is a simple method of communicating between the M6800 and the PSA. The microprocessing scheme is written in assembly language which provides for fast data acquisition and a delayed output of electrode potential versus time transients to a X-Y recorder.

### Introduction

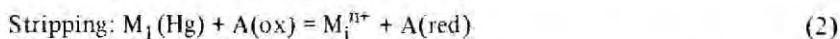
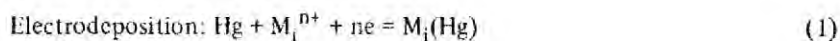
Stripping voltammetry is a well-known technique in analytical chemistry, which involves a pre-concentration (via electrodeposition) step and a redissolution ("stripping") step. The first step concentrates the analyte by at least 100- to 1000-fold, depending upon the length of deposition time. The analytical measurement occurs during the stripping step: typically, a linearly varying potential is applied (either in the anodic or cathodic direction), which results to the redissolution of the deposited material.

The stripping procedure, however, can alternatively be carried out in a non-faradaic mode, i.e., *chemically*, via a suitable redox reagent in solution. Though an earlier technique (called chemical stripping analysis) has been reported by Bruckenstein and Bixler (1) in 1965, potentiometric stripping analysis (PSA) of trace heavy metals was described by Jagner and Graneli (2) only in 1976. Jagner (3) has recently reviewed the range of applications of the technique.

### Theory

There has been some attempt recently to develop the theory of PSA (4,5). Only the salient points are given here.

Consider the oxidative mode of PSA, and assume a thin mercury film on a glassy carbon substrate as working electrode. The following reactions take place:



where  $\text{M}_i$  refers to a metal,  $\text{A}(\text{ox})$  to an oxidant (stripping agent), and  $\text{A}(\text{red})$  to the reduced form of the stripping agent.

The total amount of amalgam  $\text{M}_i(\text{Hg})$  formed during the electrodeposition for a period of  $t_{\text{dep}}$  seconds is

$$C_{\text{M}_i(\text{Hg})} \propto [\text{M}_i^{n+}] t_{\text{dep}} \quad (3)$$

where  $\text{M}_i^{n+}$  refers to the bulk solution concentration of  $\text{M}_i^{n+}$ . For several oxidant forms, the total stripping time,  $\lambda$ , when  $C_{\text{M}_i(\text{Hg})} = 0$ , can be written as

$$\lambda \propto \frac{1}{\sum [\text{A}_j(\text{ox})]} \quad (4)$$

Combining equations (3) and (4) gives the analytical stripping time,

$$t_{i,\text{strip}} \propto [\text{M}_i^{n+}] \frac{t_{\text{dep}}}{\sum [\text{A}_j(\text{ox})]} \quad (5)$$

If the concentrations of  $\text{A}_j(\text{ox})$  and hence the stripping rate do not change appreciably throughout the experiment, then equation 5 simplifies to

$$t_{i,\text{strip}} \propto [\text{M}_i^{n+}] t_{\text{dep}} \quad (6)$$

Equation 6 represents the basic relationship for quantitative PSA. An equivalent expression can be written for the cathodic PSA mode, which involves an anodic pre-electrolysis followed by stripping using a reductant in solution.

Qualitative identification of the element is based on confirmation of the electrode potential predicted by the Nernst equation.

During the chemical stripping, the variation of the working electrode potential with time is recorded ("potentiogram"). An equation for this curve has also been described (4,5). A method for generating "stripping polarograms" from potentiograms has been suggested (5).

### Instrumentation

The project which will now be described involves the development of an inexpensive but sensitive PSA instrument which is microprocessor-based.

The PSA instrumentation is relatively simple. The basic requirement consists of a potentiostat, a three-electrode cell, and a high-input impedance recorder. An automated commercial system is now available but is quite expensive (3).

An analog PSA instrument which provides for both oxidative and reductive PSA modes was described by Kryger *et al.* (6). Below is a modified version of this instrument: it is microprocessor-based such that fast stripping rates on non-deoxygenated samples can be handled readily (i.e., dissolved oxygen could serve as stripping agent), and omits the analog differentiating circuit.

*Potentiostat.* Figure 1 shows the potentiostatic circuit used for electrodeposition. It includes three different relays (A, B, and C), the states of which are summarized below for the two stages of the analysis.

Item	Electrodeposition	Stripping
Relay A	ON	OFF
Relay B	OFF	ON
Relay C	OFF	ON
Potentiostat	ON	OFF
XY Recorder	OFF	ON

As in the Kryger instrument, there are two other options of applied potential values, and are indicated in Figure 1 by dashed lines. Some practical applications of the multiple applied potential sources may be found in the original paper (6).

*Interface Circuit.* The potentiostat is controlled by a Motorola 6800-microprocessor, which is available in the Heathkit Model ET-3400 microcomputer learning system. The circuit was built on protoboards which facilitated circuit modifications. The present circuit is given in Figure 2.

Two peripheral interface adapters (PIA) are employed in the communication system between the PSA and the microprocessing unit (MPU). The PIA has the advantage of requiring fewer IC chips. PIA-1, port A is configured as an input, and an eight-bit analog-to-digital converter (ADC) is connected to this port, the MPU reads data from the PSA via this port. PIA-1, port B is configured as an output; three of the eight lines are used to turn the relays ON and OFF. Both ports of PIA-2 are configured as outputs: port A is connected to a digital-to-analog converter (DAC) and drives the x-axis of an Hewlett Packard XY recorder, while port B is connected to another DAC which drives the recorder's y-axis. The electrode potential versus time measurements stored in the MPU are obtained as delayed output to the recorder.

The cost incurred in the construction of the potentiostat was only approximately U.S.\$160.00. The microchips and other electronic components for the interface circuit were available from the Heathkit system, which is used in an instrumentation course offered by the Chemistry Department to advanced chemistry majors.

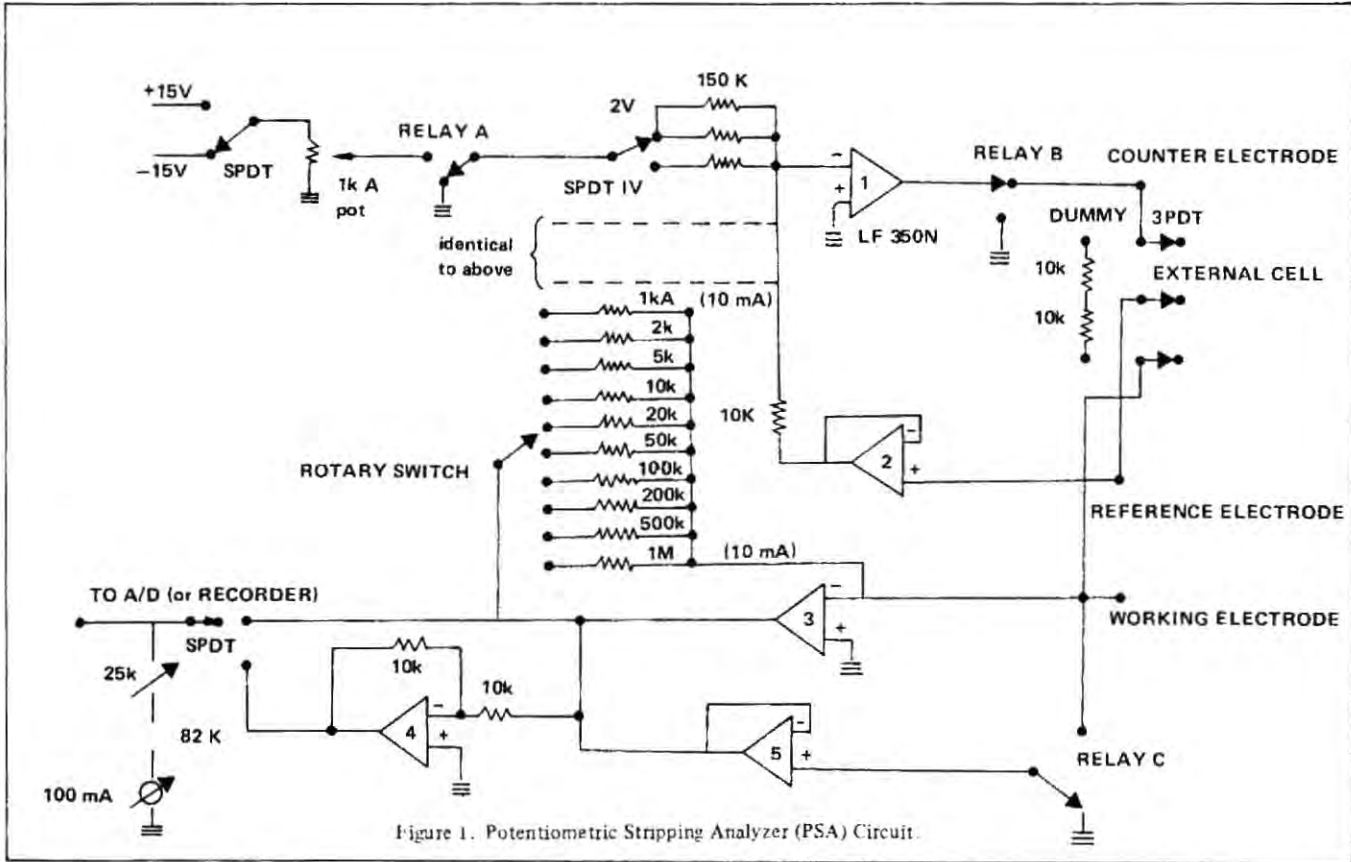


Figure 1. Potentiometric Stripping Analyzer (PSA) Circuit.

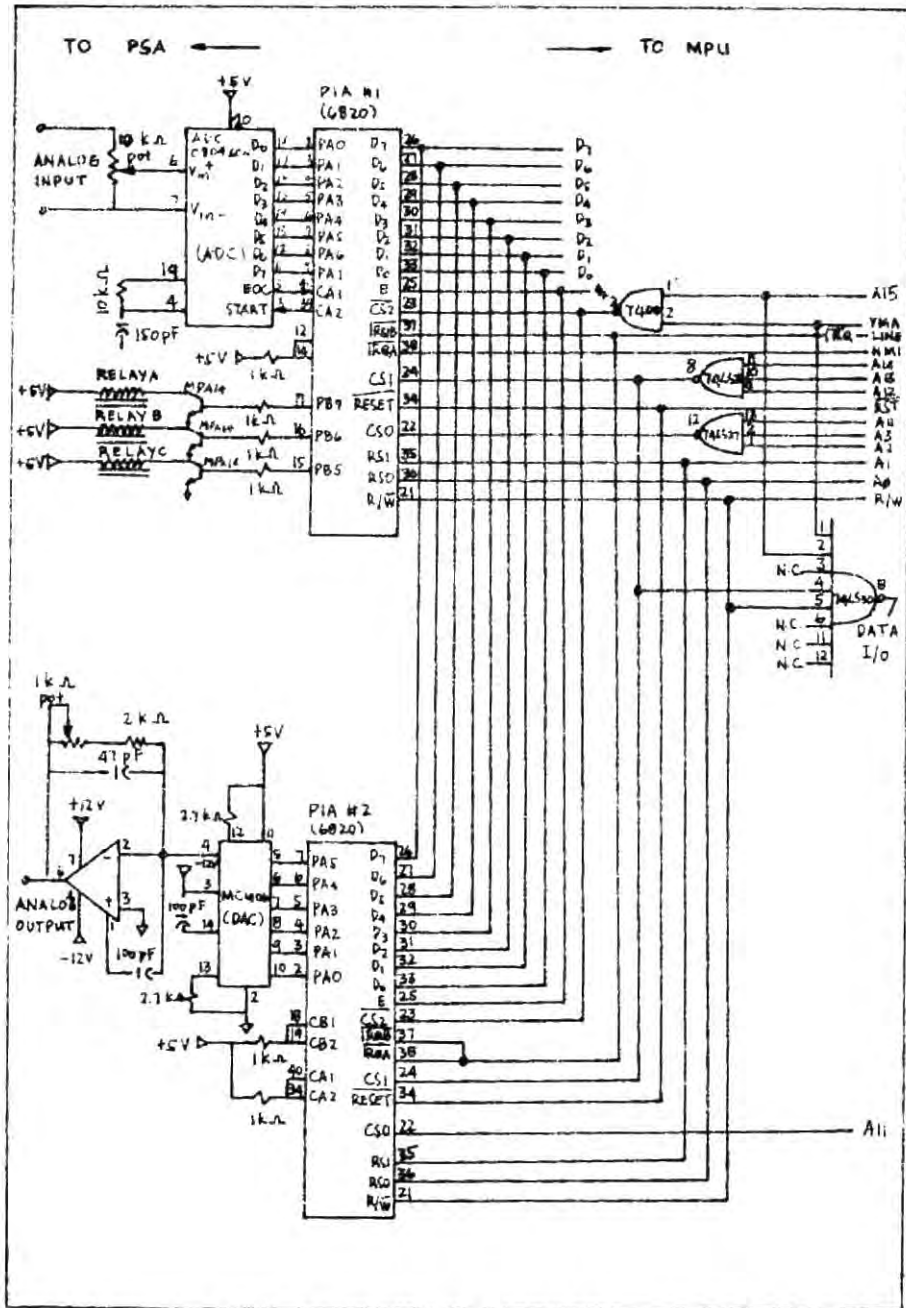


Figure 2. Interface Circuit.

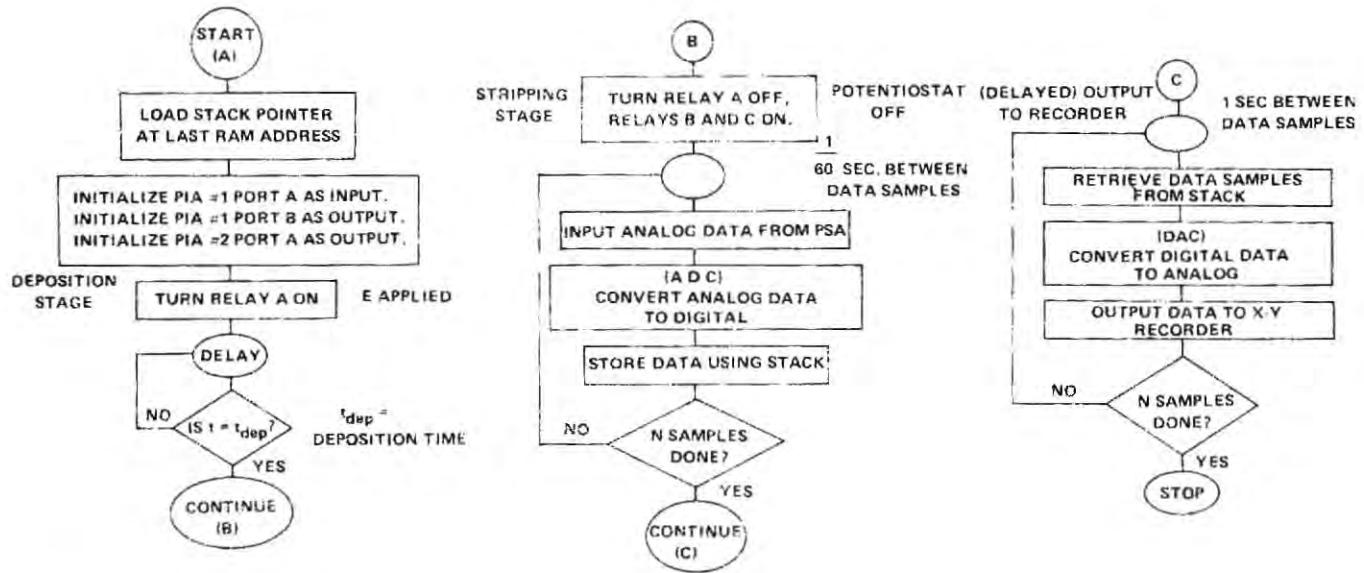


Figure 3. Microprocessing Scheme.

### Preliminary Results

**Microprocessing Scheme.** Figure 3 gives the microprocessing scheme for the electrodeposition step, the stripping stage, and the delayed graphic output to the recorder. The program is written in assembly language to enable rapid acquisition of data. Using the MPU built-in clock (60 Hz), one data sample is read every 17 milliseconds.

**Typical Potentiogram.** The microprocessor-controlled instrument was tested on a non-deaerated standard solution of cadmium(II) and sample potentiograms are given in Figure 4. Curve A is a direct PSA output of the analog stripping curve (i.e., MPU is omitted); Curve B is the delayed display of data gathered by the MPU. The ideal potentiogram is depicted in the inset.

It is obvious from Curve A, Figure 4 that an analog set-up alone is not fast enough to record the electrode potential versus time transients, the electrode potential in the curve is observed to start at -0.1 volt, indicating that the stripping of

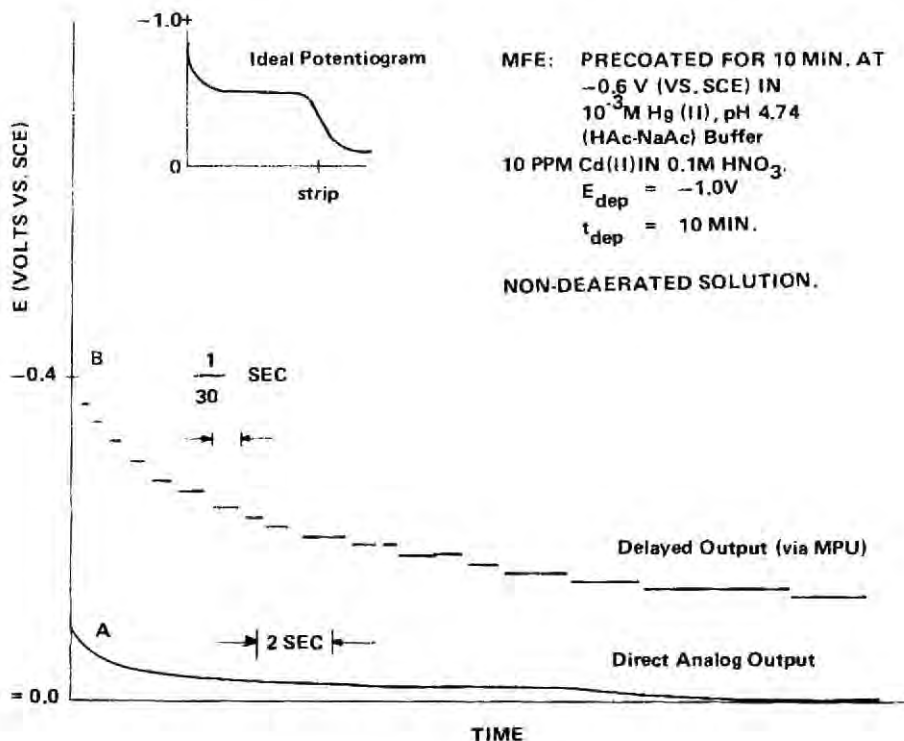


Figure 4. Electrode Potential Versus Time Transients.

cadmium is practically complete. The MPU-controlled output (Curve B) is seen to be an improvement, with the stripping curve getting recorded from -0.4 volt. It is concluded that the clock rate has to be modified and increased to one data sample read every millisecond in order to detect very low levels of analyte or fast stripping rates.

### Future Work

Refinements on the clock circuit are on-going. Conversion to a 6502-micro-processor-based system, wherein data sampling in assembly language is a subroutine of a more versatile BASIC program, is being pursued. A hard-wired general purpose interface board has been built according to McKerrow's design (7), and can be used with a 6502-MPU such as the Apple II. Analytical stripping times will be determined by a derivative technique that will be implemented by software rather than by an analog differentiating circuit, which tends to suffer from too much electrical noise. Finally, the PSA technique will be applied to the study of trace metal speciation (8) in natural freshwater systems.

### Acknowledgments

V.A.V. gratefully acknowledges support from the Australian Universities' International Development Program (I.D.P.) during a three-month study visit in 1984 at Deakin University (Waurin Ponds, Victoria, Australia) to undertake part of this project.

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