

APPLICATION OF AN AUTORANGING AMPLIFIER IN THE SIMULTANEOUS DETERMINATION OF TRACE HEAVY METALS BY ANODIC STRIPPING VOLTAMMETRY

SAM BEN-YAAKOV

Department of Electrical Engineering, Ben-Gurion University of the Negev,
Beer-Sheva, Israel

and

BOAZ LAZAR

Department of Geology, The Hebrew University, Jerusalem, Israel

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Summary—An autoranging amplifier with a gain of 1–1000 is described, together with its possible application in anodic stripping voltammetry. The performance of the amplifier is demonstrated by differential-pulse anodic stripping voltammetric analysis of stored sea-water, in the subtractive mode with two working electrodes. It is suggested that the autoranging amplifier could save considerable analysis time by eliminating the need for trial runs for gain adjustments and by relieving the operator from the need to change the recorder scale during the analysis.

Anodic stripping voltammetry (ASV) and in particular differential pulse ASV (DPASV) have recently received much attention because of their great sensitivity for several metals of environmental concern.^{1–6} Advantages of the method are that little or no sample preparation is required, and that a number of species, notably Zn(II), Cd(II), Pb(II) and Cu(II), can be determined simultaneously.⁷ Determination of each is based on measurement of the height of the current peak (i_p) recorded during the stripping phase, since this is proportional to the concentration.⁸ The stripping current is normally transformed into a corresponding voltage signal and recorded on a strip-chart recorder. Simultaneous determination by ASV or DPASV of several metals at widely differing concentrations will necessitate changing the recorder scale during the analysis, which therefore requires the undivided attention of the operator, especially when the concentrations are unknown or cover a wide range. Consequently, the conventional procedure often involves one or more trial runs to determine the range changes required. This difficulty has been overcome by us by using the autoranging amplifier described here. It was found that in most applications the amplifier completely eliminated the need for a range change during a run, thereby saving considerable analysis time in two ways: no trial runs are required and the operator is free to attend to other tasks such as the preparation of the next sample.

Although at present used manually, the autoranging amplifier was designed to be used eventually in an automatic monitoring system, in which case, the device can simplify the data-acquisition system by making possible the use of a low-resolution, and

hence low-cost, analogue-to-digital converter (ADC), even when an extremely wide dynamic range is expected. This can be achieved by reading into the data-acquisition system both the digitized signal and the gain of the autoranging amplifier. Since the gain range is from 1 to 10^3 , the equivalent dynamic range of the system when a 10-bit ADC is used is about 20 bits.

Although originally designed and at present used for DPASV the autoranging amplifier could be useful in other instrumental methods which require the handling of large dynamic range signals, *e.g.*, gas chromatography.

Data compression could also be achieved by non-linear conversion, *e.g.*, by use of a logarithmic amplifier.⁹ However, the autoranging amplifier has a number of practical advantages over a logarithmic amplifier. Since data are handled linearly there is no need for special (logarithmic) recording paper. Also, automatic data-handling is simpler because data-manipulation can be done directly without the need for an additional conversion back into linear form.

PRINCIPLE OF OPERATION

The autoranging amplifier (Fig. 1) comprises a programmable-gain amplifier and associated circuitry for automatically changing the gain of the amplifier when the output signal is outside a given amplitude range. The gain is increased or decreased in a stepwise manner when the output signal is smaller or larger than a predetermined level, respectively. This is accomplished by comparing the output signal to the

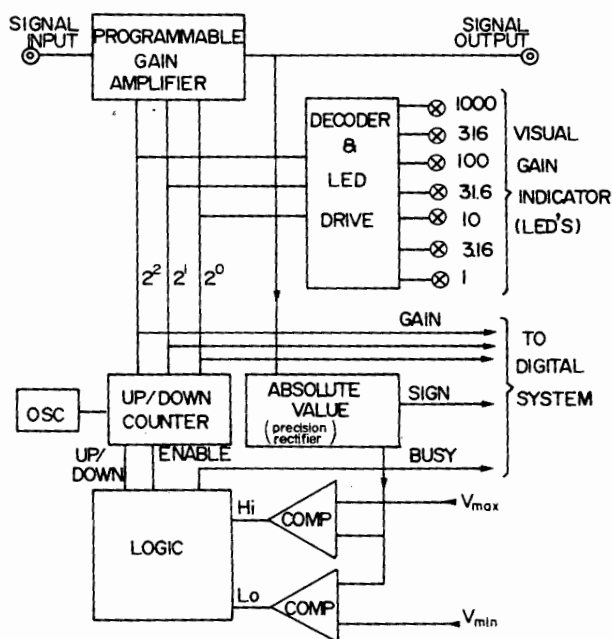


Fig. 1. Block diagram of the autoranging amplifier.

maximum (V_{max}) and minimum (V_{min}) levels permissible and applying a decrement or increment to an up-down counter whenever the output signal is outside the desired amplitude range. Since the state of the counter determines the gain of the amplifier, the output signal will always be maintained within the required range as long as the dynamic range of the device is not exceeded.

The gain increments are set so that each represents a factor of $\sqrt{10}$, i.e., 3.16 for one step and of 10 for two steps. Since the lower limit (V_{min}) is set to approximately $0.3 V_{max}$, the output signal will always be larger than $0.3 V_{max}$ except when the highest gain (1000) is reached and the input signal is smaller than $0.0003 V_{max}$. If V_{max} is set to full scale (FS) on the strip-chart recorder, the recorded trace will thus always be kept in the region (0.3–1.0) FS except when the signal is too low, as indicated above, or larger than V_{max} .

Bipolar operation is made possible by basing the automatic gain adjustment system on the absolute value of the signal (Fig. 1). In the bipolar mode, the recorder pen is set to mid-scale for a zero-level signal and V_{max} is adjusted to 0.5 FS. The autoranging amplifier will then keep the trace on-scale except when the signal level exceeds $|V_{max}|$. For example, if the recorder FS is 10 V and V_{max} is 5 V, the autoranging amplifier will handle and permit the continuous recording of signals in the range ± 5 V with a maximum sensitivity of ± 5 mV. Furthermore, since each gain increment represents a factor of 3.16 the minimum shift of the recorded trace will be ± 0.3 FS except when the absolute amplitude of the signal is

smaller than about 1.5 mV (corresponding to 0.3 FS at the highest sensitivity).

The voltage gain of the amplifier at any instant is displayed by LED indicators and is available as a TTL-compatible digital signal for use by the automatic data-handling system (Fig. 1). An additional line, BUSY, is used for indicating a transient state following a gain change, when the output data may not be valid. A complete circuit diagram of the autoranging amplifier is given in Fig. 2.

EXPERIMENTAL

Instrumentation

Measurements were made with a Ben-Gurion University (BGU) Model EI224 Polarographic Analyser equipped with a BGU Model IL06 Autoranging Amplifier and recorded with a Perkin-Elmer Model 56 strip-chart recorder. The polarographic analyser was developed by one of the authors (S.B-Y) and built at the Department of Electrical Engineering of BGU. It can be operated manually or under computer-control, and is capable of performing linear-sweep, pulse and differential pulse ASV. The option of using two working electrodes for subtractive ASV,¹⁰ which enhances the stripping peaks by subtracting the background, is also built in.

When operating in the differential pulse mode, as applied here, the polarographic analyser uses a staircase waveform on which a pulse is superimposed (Fig. 3). This pulse form is similar to the one recently investigated by Turner *et al.*¹² and found to increase the sensitivity. In this work the subtractive mode was used, similar to the procedure described by Sipos *et al.*^{10,11} except that we applied the final potential to the second working electrode for the last 10 sec of the plating time.

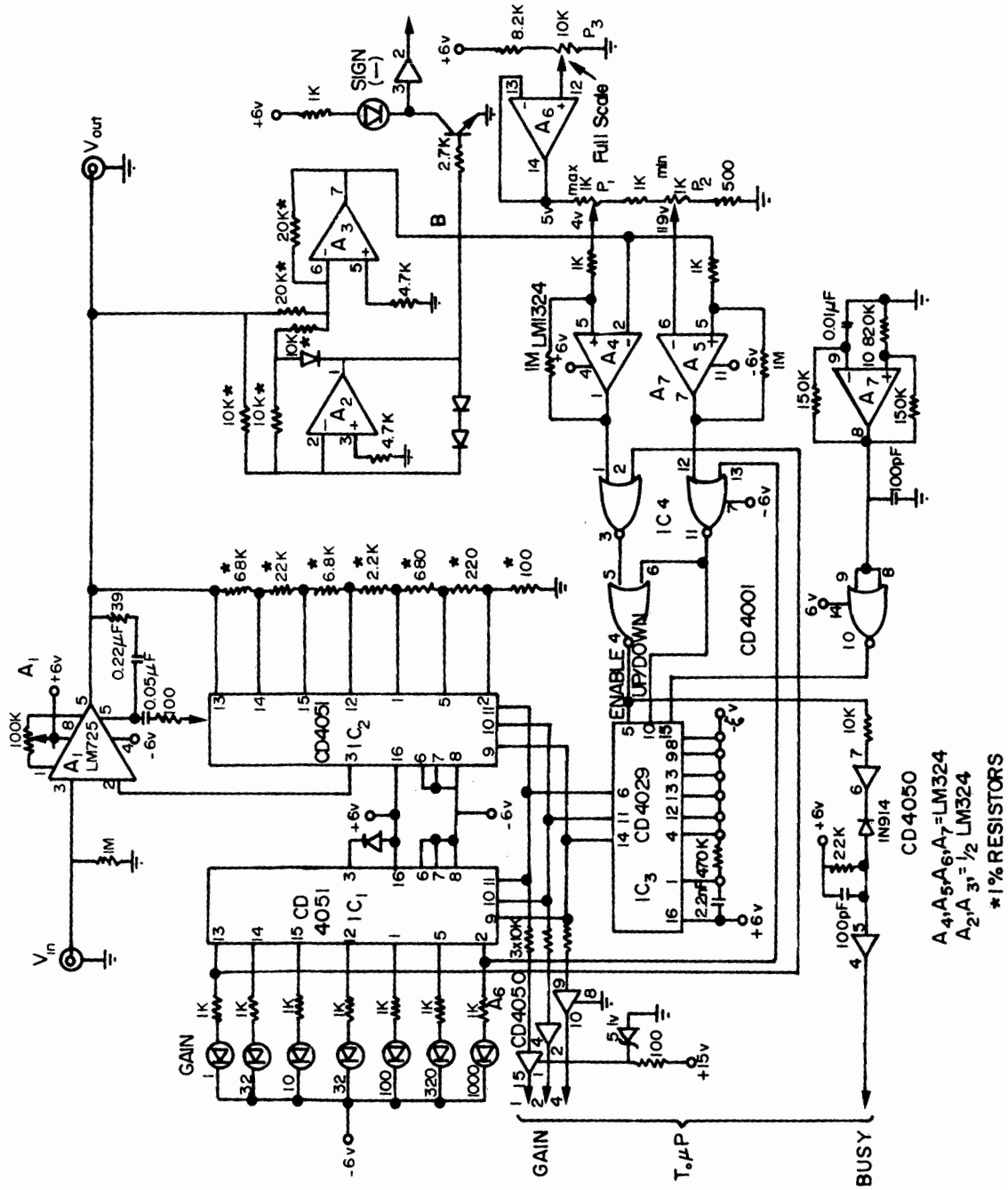


Fig. 2. Complete circuit diagram of the autoranging amplifier.

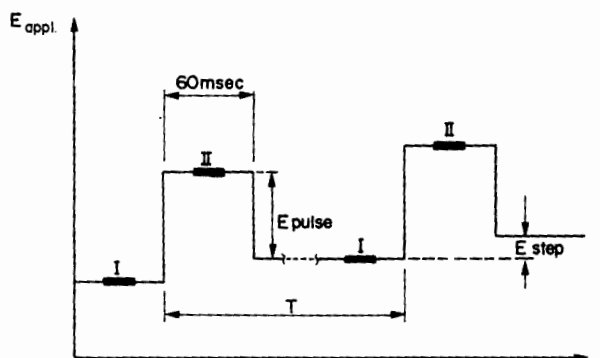


Fig. 3. Pulse shape used during the stripping phase of the DPASV analysis. Current samples are integrated over the periods marked by the heavier lines. The output signal of the polarographic analyser is proportional to the difference between the two integrated currents ($\int_{II} i dt - \int_I i dt$). In the present analysis $E_{step} = 10$ mV; $E_{pulse} = 80$ mV; $T = 640$ msec.

Electrodes and cell

Measurements were made in a 100-ml Teflon beaker fitted with a Teflon cover through which the electrodes and the tube carrying the purge gas (CO_2) were inserted. The solution was stirred with a Teflon-coated stirring bar.

A Radiometer type K-401 saturated calomel electrode equipped with a Coleman fibre liquid-junction (Perkin-Elmer C 003-0702) filled with 2M potassium chloride served as reference electrode and a coiled platinum wire was used as auxiliary electrode. The working electrodes were thin mercury-film electrodes (TMFE) deposited on glassy carbon (GC) 3 mm in diameter (Ringesdorff Werke S-10). Two electrodes were included in one housing to form a double TFME (DTFME) as required for the subtractive mode.¹¹ The DTFME was constructed by cementing two GC rods, 10 mm long and 3 mm diameter, into a 'Plexiglas' disc, 14 mm in diameter and 3 mm thick. The distance between the two GC surfaces was 5 mm. A coaxial cable was attached by a conductive epoxy resin to the other side of the GC rods, and the Plexiglas disc, with the GC pieces, was glued to a Plexiglas tube (outer diameter 15 mm, bore 8.5 mm, length 150 mm) to form the DTFME. Finally, the tube was filled with epoxy cement (Buchler No. 20-8130-032 and No. 20-8132-20) to reduce the chance of errors due to surface current leakages, and to fix the coaxial cables in place.

The electrode faces were polished with Hyprez Diamond Compounds of 6, 1, and 0.1 μm grade on a Hyprod Pellon Cloth (Engis Ltd.). The surface finish was checked for scratches by inspection through a reflected-light microscope.

Reagents and solutions

Gulf of Eilat (Red Sea) sea-water sampled and stored in 15-l. containers which had been cleaned with 1N nitric acid and rinsed several times with the water sampled. Before the ASV analysis the sea-water was spiked with Zn and Cu(II) to final concentrations of approximately $2.3 \times 10^{-10}M$ Zn and $2 \times 10^{-10}M$ Cu. The spike solutions were prepared from certified atomic-absorption standard reference solutions (Fisher Scientific Company). The plating solution was approximately $2 \times 10^{-5}M$ mercuric nitrate prepared by dissolving the salt (Baker Analyzed Reagent) in sea-water. Commercial CO_2 was bubbled through vanadium(II) chloride solution, and then through

the sample during the entire analysis cycle, to remove dissolved oxygen.

Procedure

The Teflon cover, through which the electrodes were inserted, was placed on a 100-ml Teflon beaker containing the mercury plating solution and a potential of -1400 mV was applied to both working electrodes (WE) for 20 min. After the plating, the potential was changed to -100 mV for another 3 min to strip any trace metal deposited during plating. The electrodes were then rinsed with doubly distilled water and placed in the sample solution (stored sea-water). The solution was then aerated for 7 min, after which the ASV cycle was commenced. The analysis consisted of 5 steps: (1) application of -1400 mV to both working electrodes in a stirred solution for 110 sec; (2) the potential of WE_2 was changed to -100 mV for 10 sec while WE_1 was kept at -1400 mV; (3) a rest period of 30 sec for both working electrodes in unstirred solution at -1400 mV, and adjustment of the polarographic analyser to zero output current by setting of the current gain for WE_2 ; (4) scanning from -1400 to -100 mV ($E_{pulse} = 80$ mV, $E_{step} = 10$ mV, $T = 640$ msec) recording the difference in current from the two working electrodes; (5) stripping both working electrodes for 30 sec at -100 mV in stirred solution.

RESULTS AND DISCUSSION

The performance of the ASV system with an auto-ranging amplifier is demonstrated by the analysis of spiked sea-water (Fig. 4). Stored Gulf of Eilat sea-water was spiked with zinc and copper(II) to increase markedly the peak heights for these metals relative to those for cadmium and lead. Two ASV runs are shown: a normal run and one with the auto-ranging amplifier. In the conventional run, the gains of the voltammeter and recorder were kept constant during the analysis. The gain was initially adjusted to keep the large zinc and copper peaks on scale, as a result of which the much smaller cadmium peak is barely detectable and the somewhat larger lead peak is

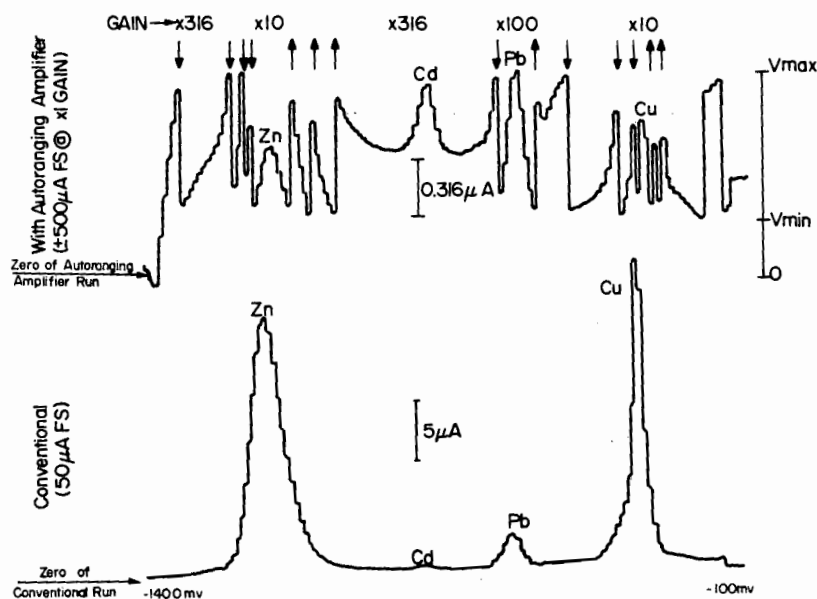


Fig. 4. SDPASV of stored sea-water. Lower trace: fixed-gain recording, upper trace: autoranging recording. Plating time: 2 min. Plating potential: -1400 mV. Pulse shape during stripping cycle: as in Fig. 2. Approximate concentrations: $Zn = 2.3 \times 10^{-7} M$; $Cd = 9 \times 10^{-11} M$; $Pb = 2.4 \times 10^{-9} M$; $Cu(II) = 2 \times 10^{-7} M$. See text for analytical procedure.

recorded with bad resolution. It should be pointed out in this connection that the subtractive mode is very effective in reducing the background current to very low levels (Fig. 4).

The upper trace of Fig. 4 was generated by repeating the analysis and using the autoranging amplifier. In this run, the recorder scale was set to a gain corresponding to a stripping current of $1000 \mu A$ FS. This gain is lower by a factor of 20 than the gain used in the conventional run. Also, the pen position was adjusted to mid-scale for zero input. V_{max} of the autoranging amplifier was set to a level corresponding to a current of approximately $350 \mu A$. It should be noted that if V_{max} had been adjusted to a level corresponding to $500 \mu A$, the trace would still have been kept on scale, and the resolution would have been somewhat better.

Although the trace generated by the autoranging amplifier seems at first complex, a closer examination reveals that it may be interpreted easily by following some simple rules. Fast pen movements are indicative of a change of scale; a trace step from a higher level to a lower level signals a decrease in gain (by a factor of $\sqrt{10}$) whereas a fast pen move from a lower level to a higher level is a result of a gain increase. Hence, once the initial gain factor is known, the gain for each section can easily be determined simply by following the gain changes as indicated by the steps. The absolute peak height is then determined by dividing peak height, measured on the chart, by the relevant gain factor. A similar approach is then used to determine the base-line level adjacent to the peak in question. The net peak height, that is the peak height above the

base-line, is then obtained as usual by subtracting the absolute base-line level from the absolute peak height.

In the trace in Fig. 4, the smallest peak current (i_p) is $0.34 \mu A$ corresponding to a cadmium concentration of about $9 \times 10^{-11} M$, as determined by the standard addition method. The largest peak is approximately $26 \mu A$, corresponding to a copper concentration of about $2 \times 10^{-7} M$. The ratio between the largest and the smallest peak currents is therefore about 75. To handle this dynamic range, the gain of the autoranging amplifier was switched from a gain factor of 316 for the smallest peak to a gain factor of 10 for the largest peak (Fig. 4). Since the inherent dynamic range of the present autoranging amplifier is larger, much larger peak-height ratios can be handled.

It should be emphasized, however, that although the autoranging amplifier simplifies the task of the operator by relieving him of the need to change scales during an analysis, the method does not in any way enhance the quality of the data or their readability. In particular, the amplifier will not enhance a small peak superimposed on the flanks of a larger peak. Nor will the amplifier circumvent the problem of a high base-line current. In such cases, the autoranging amplifier will not switch to a higher sensitivity, because it responds to the total signal and not just to the useful peak signal. Hence, the resolution of the system, when defined as the smallest detectable change in signal, is kept the same. However, the operational advantages of the autoranging amplifier could be crucial when large peak-height ratios are encountered.

The autoranging approach could also be useful in automatic systems. An alternative to this approach

would be a programmable-gain amplifier controlled by software. The two approaches are probably comparable when the analysis is controlled by a computer. However, the autoranging approach is more convenient to implement in simpler automatic systems which do not include a micro or minicomputer.

In this paper we have discussed only the problem of large dynamic range in the simultaneous determination of trace metals by ASV. This is but one of the many problems encountered when attempting to design an automatic ASV analyser. The problems of interpretation in view of the possible formation of intermetallic compounds and the problem of automatic calibration are just two additional examples of the many problems involved. Suggested solutions to these and other problems will be reported at a later stage of the present study.

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