

**DIFFERENTIAL ELECTROLYTIC POTENTIOMETRY:
INSTRUMENTATION AND APPLICATION OF
MARK-SPACE BIASED PERIODIC CURRENT
POLARIZATION IN ACID-BASE TITRIMETRY
IN DIMETHYLSULFOXIDE.**

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الخلاصة :

تم تصميم وبناء مصدر تهييج لا يحتاج الى مولد موجات تجاري وتم استخدام هذا المصدر في طريقة فرق الجهد التفاضلية ذات الحيود الزمني .
ان منحنيات المعايرة الناتجة توضح فاعلية هذا المصدر في التفاعلات الكائنة في الأوساط المائية وغير المائية ، ولقد تم التعرف على سلوك الأقطاب المهيجة في اكسيد الكبريت الثنائي الميثيل .

ABSTRACT

A polarization source which does *not* require a commercial waveform generator was designed and employed in the technique of mark-space biased differential electrolytic potentiometry. The titration curves obtained indicate the adequate performance of this source in both aqueous and non-aqueous titrimetric reactions. The behavior of polarized antimony electrodes in dimethyl sulfoxide has also been investigated.

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INTRODUCTION

Mark-space biased differential electrolytic potentiometry (m.s.b. DEP) is a method of studying electrode processes and titrimetric reactions. It consists of polarizing two identical electrodes by a mark-space biased (time biased) periodic wave and measuring the potential difference between them [1–8]. Two types of differential titration curve can occur, depending on the speed of the electrode processes concerned [1]. For fast reactions, a symmetrical peak of type I results, but if one of the electrode processes is slow then the titration curve will have the Z-shape (type II).

Bishop and Webber [1] were the first to investigate polarization with perfectly symmetrical periodic waveforms. They found that the use of a mark-space biased periodic wave destroys the periodic differential curve (E), but produces a DC component which polarizes the electrodes. The short time in which these electrodes attain their equilibrium potentials has been attributed to two factors: firstly, the repeated reversal of the signal activates the electrodes; and secondly, the total amount of the current is large [2].

Bishop and Hartshorn [2] have designed an instrument that is capable of producing a mark-space biased signal of 0 – 99% bias. This instrument requires a commercial waveform generator, a time measuring instrument and an integrator in order to

produce a symmetrical periodic wave which is time biased.

The technique of m.s.b. DEP has been applied to acid–base titrations in acetic anhydride–acetic acid mixtures [3]. It has also been applied to oxidation–reduction and precipitation titrations in anhydrous acetic acid [4,5].

End-points of titrimetric reactions in dimethyl sulfoxide (DMSO) have been obtained either potentiometrically [9] or by means of indicators such as thymol blue [10]. The technique of m.s.b. DEP has not been previously applied to titrimetric reactions in DMSO.

This paper describes a mark-space biased polarizing source which produces a symmetrical periodic wave of 0.5–99% bias *without* employing a commercial waveform generator. The performance of this polarizing source in some aqueous titrations is also described. The results of a study of the applicability of m.s.b. DEP to acid–base titrations in DMSO are also reported.

EXPERIMENTAL

The polarizing source which produces the time biased square wave was designed and constructed as shown in Figures 1 and 2. Figure 1 represents a DC power supply source which is powered from the main AC supply with 110 V/ 60 Hz via the step down

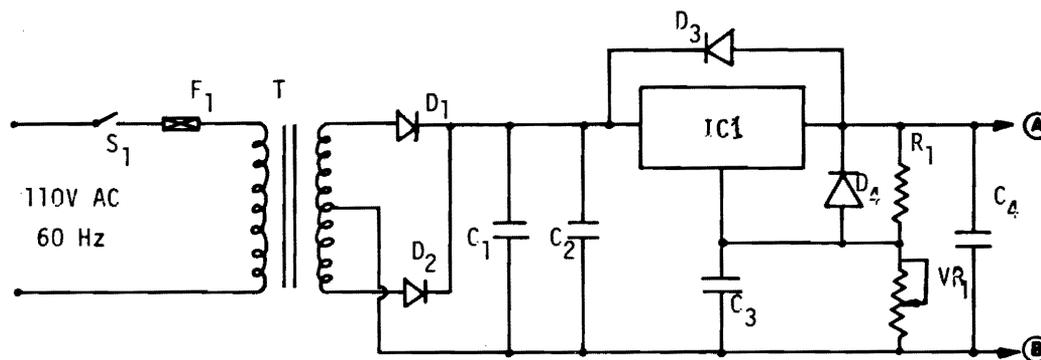


Figure 1. Power supply. S_1 = switch SPST 125 V, 2A. F_1 = fuse 300mA. T = transfer primary 110 V, 60 Hz; secondary 12-0-12 V, 500 mA. IC_1 = integrated circuit LM317 T. Diodes D_1 , D_2 : IN4001; D_3 , D_4 : IN4002. Capacitors C_1 : 2200 μ F, 25 WV, Electrolytic; C_2 : 0.1 μ F, 50 WV, Ceramic; C_3 : 10 μ F, 25 WV, Electrolytic; C_4 : 1 μ F, 25 WV, Electrolytic. Potentiometer VR_1 : 5k Ω .

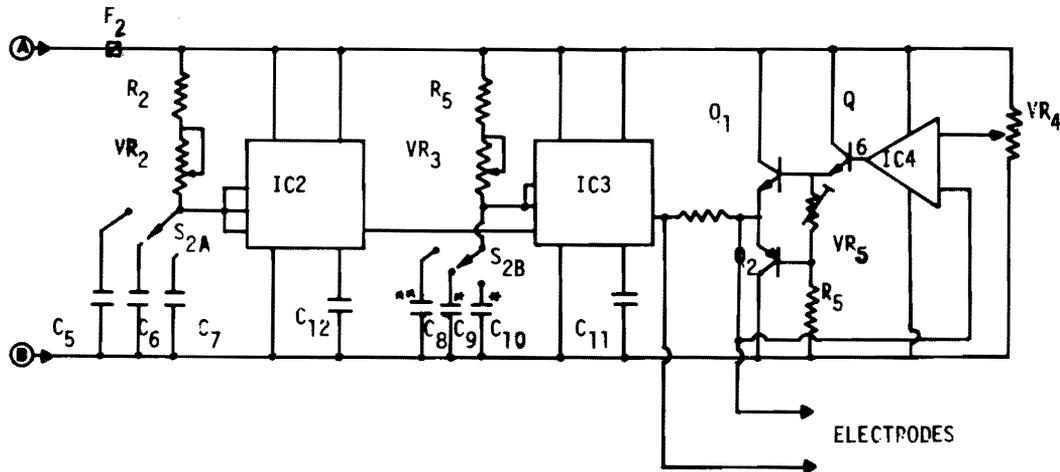


Figure 2. Waveform generator. $F2 =$ fuse 500 mA. Capacitors $C5, C8$: 10 μF , 25 WV, solid tantalum; $C6, C9$: 0.1 μF , 50 WV, Mylar; $C7, C10$: 0.01 μF , 50 WV, Mylar; $C11, C12$: 0.01 μF , 50 WV, Ceramic. Integrated circuits $IC2, IC3$: LM555; $IC4$: 741CP. Potentiometers $VR5$: 5k Ω ; $VR2, VR3$: 1 M Ω ; $VR4$: 50 k Ω . Resistors $R2, R3$: 1 k Ω , $\frac{1}{2}$ W; $R4$: 2.2 k Ω , $\frac{1}{2}$ W; $R5$: 4.7 k Ω , $\frac{1}{2}$ W. Frequency range selector switches $S2A, S2B$: DPTT rotary. Fuse $F2$: 500 mA. Transistors $Q1$: BD 131, $Q2$: 132, $Q3$: BC 108.

transformer T. The output of this transformer is connected to a rectifying and filtering unit which consists of the diodes D1 and D2 as well as the capacitors C1 and C2. This unit converts an AC voltage into a DC voltage. The latter is then applied to an integrated circuit IC1 which is considered as a positive voltage regulator. This integrated circuit was selected primarily to provide a constant DC voltage and to control the amplitude of the output waveform. The reference input of this circuit (IC1) is provided at its control input by means of the resistor R1 and the capacitor C3. Diodes D3 and D4 are used for the protection of IC1 against transients. The potentiometer VR1 is used to vary the output from 5 V p-p to 15 V p-p.

Figure 2 shows the circuit which acts as a waveform generator. It includes two similar integrated circuits IC2 and IC3. The first integrated circuit IC2 operates in an astable mode and produces the output waveform of the required frequency. The second integrated circuit IC3 operates in a monostable mode and controls the duty cycle (mark-space ratio) of the output. These two integrated circuits were selected because of their relatively fast rise and fall times. Moreover, they are able to source and/or sink a current which is greater than 100 mA through the load and at the same time achieve a high degree of timing accuracy.

A timing RC network for the integrated circuit IC2 is formed by the series combination of the resistor R2, the potentiometer VR2 and one of the capacitors

C5, C6, or C7 which is selected by the switch S2A. The period of the waveform is variable. It can be changed from 10 ms to 12.5 ms by means of VR2 and the selector switch S2A. The output of IC2 is applied as a trigger input for the integrated circuit IC3. Once IC3 is triggered, the output conducting time which contributes to the duty cycle is altered through VR3 from 0.5% to 99% of the period. To limit the duty cycle to some fixed value within the range 0.5%–90% of the output wave, IC3 is incorporated into an RC network. This network includes the potentiometer VR3 in series with the resistor R3 and one of the capacitors C8, C9, or C10. The appropriate capacitor (C8, C9, or C10) is automatically selected through the switch S2B which is ganged to S1A. The integrated circuit IC4 senses the voltage at the junction of transistors Q1/Q2 and compares it with the required base line reference. The latter is fixed by means of the potentiometer VR4. The output of IC4 is applied to the transistor Q3 which acts as a buffer amplifier and drives the complementary transistor pair Q1/Q2. The potentiometer VR5 together with the resistor R5 controls the conduction of Q1 and Q2, thereby limiting the maximum output current to 100 mA. The electrodes are connected across R3, which is a bleeding resistor.

The complete circuit shown in Figures 1 and 2 was mounted in a metallic chassis. All the controls to vary the output amplitude, the percentage bias, the current offset and the frequency were provided on the front panel of the chassis. A selector switch

(single pole/six throw) that allows zero-current potentiometry to be performed was mounted over the chassis. This arrangement allows a comparison between m.s.b. DEP and zero-current potentiometry. The output amplitude and the symmetry of the periodic wave were observed by means of a Tektronix 475 oscilloscope. The frequency and the percentage bias were measured by a universal counter (5315 A Hewlett-Packard). The instruments required for monitoring the output parameters were connected to the terminals provided at rear panel of the chassis. The titration cell, the preparation of both platinum and antimony electrodes, the calculation of the percentage bias and the general experimental procedure have all been previously described [1–3,6].

A non-aqueous double bridge [3] was employed to avoid the direct contact between the aqueous salt

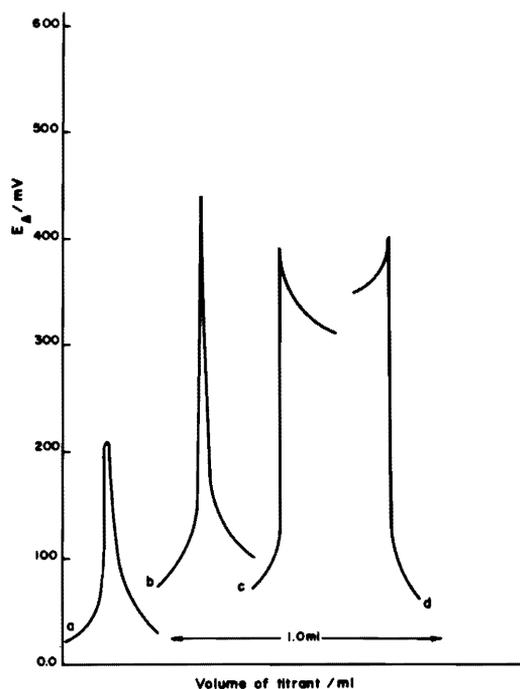


Figure 3. Titration curves obtained under the following conditions in aqueous media: percentage bias = 10%; rms current density = $20 \times 10^{-6} \text{ A cm}^{-2}$; frequency = 50 Hz. Curve a: titration of 10 ml of 0.0125 M perchloric acid with 0.05 M barium hydroxide using antimony electrodes.

Curve b: titration of 10 ml of 0.0125 M iron(II) in 0.5 M sulfuric acid with 0.10 M cerium(IV) using platinum electrodes.

Curve c: titration of 10 ml of 0.01667 M bromate with 0.05 M arsenic(III) oxide in 1 M hydrochloric acid using platinum electrodes.

Curve d: titration of 10 ml of 0.05 M arsenic(III) oxide with 0.01667 M bromate.

bridge and the non-aqueous solution in the titration cell. This bridge was prepared by dissolving about 10 g of anhydrous lithium perchlorate in 65 ml DMSO, then 20 g of agar was added with continuous stirring. This solution was heated gently and after it became clear it was transferred to the Y-shaped tube [3]. The non-aqueous double bridge is used when both classical potentiometry and m.s.b. DEP are performed simultaneously. This arrangement allows the results of m.s.b. DEP to be compared with those of classical potentiometry.

All of the chemicals used in this work were of analytical reagent grade unless otherwise stated. The preparation of aqueous solutions of 0.0125 M perchloric acid, 0.05 M barium hydroxide, 0.10 M iron(II) in 0.5 M sulfuric acid, 0.10 M cerium(IV) in 0.5 M sulfuric acid, 0.05 M arsenic(III) and 0.016 M potassium bromate have already been described [1,6]. The commercially available DMSO (99% pure; BDH Chemicals Ltd.) was kept over 0.5 nm molecular sieves (30 g/l) for a prolonged period of time with intermittent stirring. To prevent contamination with water from air, the solvent was stored in a sealed container fitted with an automatic burette from which it could be dispensed under pressure from pure nitrogen gas. A 0.01 M solution of each of the following compounds was prepared by dissolving the required amount of the pure compound in DMSO and diluting to 100 ml. These compounds were: toluene-*p*-sulfonic acid, *p*-nitrobenzoic acid, anthranilic acid, ammonium chloride, ammonium nitrate, cadmium nitrate, lead nitrate, nickel chloride, and zinc chloride. A 0.05 M solution of lithium perchlorate was prepared by dissolving the required weight in DMSO. This solution was used as a supporting electrolyte. The preparation of sodium methoxide in toluene-methanol mixture has been described elsewhere [7].

RESULTS AND DISCUSSION

The performance of the mark-space polarizing source was examined by carrying out certain titrations which result in two types of differential curves, I and II [8]. These titrations include acid-base and oxidation-reduction reactions in aqueous media. Figure 3 illustrates the results of these titrations. It can be seen that the differential curve 3a, resulting from titrating perchloric acid with barium hydroxide using antimony electrodes, belongs to type I [8]. This type usually takes the form of a sharp symmetrical peak and its tip represents the end-point. The

titration curve of Fe(II) with Ce(IV) which is shown in Figure 3b also belongs to this type. The sharpness and symmetry of these differential curves indicate the normal behavior of the electrodes which were polarized by the time biased periodic wave.

Differential curves of type II (Z-shaped) were obtained from arsenic(III) oxide—bromate titration by using, first the reductant and then the oxidant as a titrant. When the reductant, arsenic(III) oxide, was used as a titrant, a rising-Z form was observed. This differential curve is shown in Figure 3c. On using bromate, the oxidant, as a titrant, a falling-Z form was obtained as presented in Figure 3d.

Several compounds were titrated in DMSO by using sodium methoxide as a titrant and antimony electrodes as indicating systems. The techniques of potentiometry and m.s.b. DEP were performed simultaneously. This arrangement allows the end-points which are obtained from m.s.b. DEP to be compared with those of potentiometry. The results of the successful titrations are given in Figure 4, where a_1 through e_1 represent the potentiometric titration curves. The corresponding differential curves which result from m.s.b. DEP are represented by a_2 through e_2 .

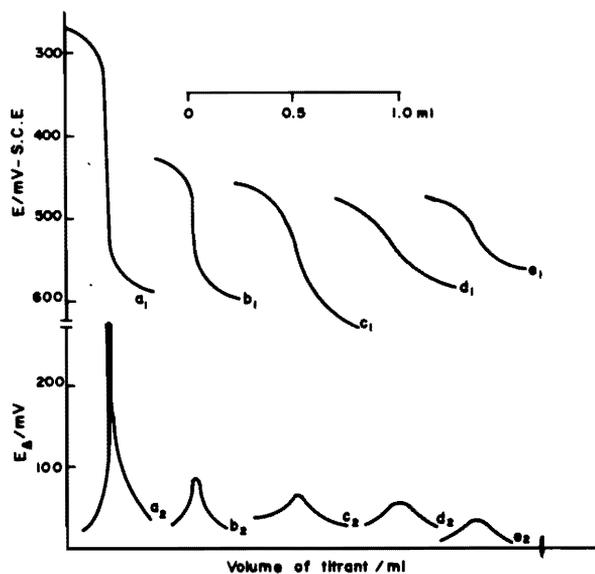


Figure 4. Potentiometric and the corresponding differential curves obtained in DMSO. The percentage bias = 10%. The rms current density = $10 \times 10^{-6} \text{ A cm}^{-2}$. Curve a_1 is the potentiometric titration curve of 10 ml of 0.01 M toluene-*p*-sulfonic acid with 0.1 M sodium methoxide using antimony electrodes. Curves b_1 , c_1 , d_1 , and e_1 are, respectively, the potentiometric titration curves of *p*-nitrobenzoic acid, *n*-phenyl anthranilic acid, ammonium chloride and ammonium nitrate. Curves b_2 , c_2 , d_2 , and e_2 are the corresponding differential curves.

Toluene-*p*-sulfonic acid acts as a strong acid in DMSO. This is obvious from its potentiometric curve a_1 which shows a sharp break. Its differential curve a_2 takes the form of a sharp symmetrical peak, characteristic of fast electrode reactions. The shapes of these curves also indicate the normal behavior of antimony electrodes in DMSO. The results of *p*-nitrobenzoic acid shows that this acid has a considerable strength in DMSO. Its potentiometric curve b_1 is fairly sharp and its differential curve b_2 is smooth and symmetrical. *n*-Phenylanthranilic acid is less acidic in DMSO than *p*-nitrobenzoic acid. The potentiometric curve c_1 of the former acid is not sharp and the height of its differential curve c_2 is small. The end-point, however, can be easily located from c_2 .

Attempts were also made to titrate some salts which may have acidic characters in DMSO. These salts include: cadmium nitrate, lead nitrate, ammonium nitrate, zinc chloride, nickel chloride, stannous chloride, and ammonium chloride. The only two salts that were found to exhibit a slight acidic behavior in DMSO are ammonium chloride and ammonium nitrate. Their titration curves are shown by d_1 , d_2 , and e_1 , e_2 , respectively. It is clear that the potentiometric curves d_1 and e_1 show no sharp inflections. Hence, they cannot be used to locate the end-points. However, the end-points of these titrations can be easily located from the differential curves d_2 and e_2 by extrapolating the straight sides of each curve. This is one of the advantages of the m.s.b. DEP technique. The other advantage is an enhanced response speed of the polarized electrodes. For instance, the time required for the zero-current electrode to reach equilibrium was found to be long during these titrations. In the vicinity of the end-point, more than 20 minutes were required to reach an acceptable drift rate of 1 mV/min. In case of m.s.b. DEP, however, the electrodes were found to equilibrate within 4 minutes or less. This is because of the high current densities employed and also because of the continual reversing of the signal which prevents the formation of oxide layers on the surfaces of the electrodes [1].

Finally, the analytical validity [1,3,5] and the reproducibility of the m.s.b. DEP method was investigated. Six identical samples of toluene-*p*-sulfonic acid solution were titrated under similar conditions. A standard deviation of 0.015 ml was obtained in a typical total volume of 50 ml. This value falls within the range expected from other methods of high precision titrimetry.

CONCLUSIONS

A polarization source which does not require a commercial waveform generator was designed and constructed. This source produces a time-biased square wave which is employed in the technique of mark-space biased differential electrolytic potentiometry. The performance of the source was examined in both aqueous and non-aqueous titrimetric reactions. For the first time, the behavior of polarized antimony electrodes in dimethyl sulfoxide has been investigated. The technique of mark-space biased DEP offers improvement over classical potentiometry in the ease of location of the end-point as well as in the enhancement of the response speed of the electrodes.

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