

A HIGH FREQUENCY OSCILLATOR BASED AUTO-TITRIMETRIC METHOD FOR REDOX SYSTEMS

M. Jaffar*

Department of Chemistry
Quaid-i-Azam University
Islamabad, Pakistan

and

M. Ishaq Sajjad, Jamil A. Tariq and S. Noorullah Hussaini

RIAD-Pinstech
Islamabad, Pakistan

الخلاصة :

طور أسلوب (الايوسيلوميتر) الاوتوماتيكي لتحديد نقاط التعادل في محاليل (ريدوكس) المائية كدالة للمحلول المعايير. ويستغل هذا الأسلوب الذبذبات التيارية في دائرة كهربائية من الترانزستور تنذبذب في (110) ميغا هرتز للتسجيل الاوتوماتيكي لمختلف عمليات المعايرة. وأوضحت الطريقة إفادة وتطبيق هذا الأسلوب باختيار مختلف أنظمة الاكسدة والاختزال في محيط مائي في تراكيز تتفاوت فيما بين (10^{-3}) الى (10^{-6}) مول. أما مجمل الخطأ فانه يقدر بحوالي $(\pm 1.1\%)$ وبدقة أحسن من $(\pm 1\%)$ في القياسات المماثلة ريدوكس (اكسدة اختزال). ويمكن أن يستخدم هذا الأسلوب في التحليلات التقديرية للتغيرات في طريقة معايرة محاليل المركبات المعقدة وفي تغيرات المنفذية الكهربائية.

ABSTRACT

An auto-oscillometric technique has been developed for tracing the equivalence points in aqueous redox estimations as a function of titrant volume. The technique utilizes the current impulses generated in a transistorized circuit oscillating at 110 MHz for the auto-recording of the titration events. The usefulness and application of the technique is demonstrated by selecting various reduction-oxidation systems in aqueous phase at concentrations ranging between 10^{-3} to 10^{-6} M. The overall error is rated at about $\pm 1.1\%$ with a precision better than $\pm 1\%$ for replicate measurements on a given redox system. This technique has the potential of application for analytical estimations related to compleximetry and permittivity changes.

*To whom correspondence should be addressed.

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INTRODUCTION

Over the past several years rapid advances in the field of electronics have provided new shape and refinement to most analytical instruments used frequently in laboratories. These advances include new operational flexibilities and incorporate automatic functioning characteristics. Consequently, both reliability and precision have improved due to improved circuit designs based on modified components warranting high sensitivity. This is also specifically true about the aqueous phase redox titrimetric technique.

An earlier development in the field was based on a Wheatstone bridge design. Conductance cells were developed and the electrode polarization resistance was studied as a function of frequency [1]. Automatic titration process based on such innovation was suggested by Gordon and Farquharson [2, 3]. A semi-automatic subtractor of titration curves, with a versatile curve-plotting device, was introduced as early as 1957 [4]. In the years to follow, similar systems with minor modifications and improvements were introduced [5, 6]. In 1963, a differential amplifier was used for the first time to detect the "end-point" of titrations [7]. Boardman and Warren [8] developed an automatic conductance titrimer, specifically for work in non-aqueous media. Another conductometric arrangement was later described [9, 10] for conventional conductometric application with the titrant added intermittently. The parallel RC-circuit for measuring solution conductance was introduced by Evans and Matesich [11]. In later developments, conductometric parameters were used for studying the reaction kinetics of moderately fast chemical reactions [12]. Bipolar pulse conductance technique [13] was used as a detector in ion-chromatography and as a phase selective technique to evaluate reference electrodes for use in non-aqueous solvents [14].

Many currently available commercial instruments operate at low frequency thus making it difficult to assess possible errors associated with electrode polarization in a bridge circuitry. Parasitic effects lead to an apparent increase in the resistance resulting from polarization and capacitive shunt. An attempt, therefore, was made in the present work to use a high frequency oscillator circuit to trim down these effects to the minimum so that a higher quantitative accuracy could be obtained in redox analytical work.

EXPERIMENTAL

A high frequency based circuit (shown in Figure 1) has been designed and fabricated to provide a means of measuring or cancelling any change in conductance cell capacitance consequent upon the addition of an oxidant or reductant in aqueous phase. The high frequency source greatly reduces the extent of electrolysis and polarization. The signal from the circuit after proper amplification is fed directly to a millivolt, multispeed potentiometric recorder. The frequency of the oscillator is rated at 110 MHz and it is found by way of comparison with low frequency oscillators (Hewlett-Packard 200 II) that concentration polarization is the least at this frequency. The stray capacitance problem at this high frequency is, however, controlled by using very short leads and mounting the circuit components so that mechanical movement could not affect oscillator stability. The high frequency cell is a cylindrical pyrex glass tube (200 mm × 40 mm) capable of holding about 60 ml solution and has two aluminum plates (1.5 mm thick, 2.5 cm apart) forming a capacitor in the immediate proximity of the tube. It affords a two terminal connection to the outer circuit by means of a coaxial cable of matched characteristic impedance. The conductivity cell ($k = 0.76 \text{ cm}^{-1}$) forms one arm of the high frequency oscillator circuit, while a standard resistance with two capacitors in series and parallel network form the second arm. The third arm consists of a network of a parallel resistance and capacitance. The fourth arm consists of a network of a capacitor with two resistances in series and parallel (Figure 1). Thus, the arrangement is a four-ganged variable capacitor circuit operating at a high frequency. The recorder is connected as per schematic of Figure 2, where details on auxiliary attachments are provided. For the balanced mode, the following condition then holds: $R_{\text{cell}}/R_2 = R_3/R_4 + C_4/C_3$. The resistance of the dip-cell (R_{cell}) can be calculated since the values of other quantities are known. The high frequency oscillator can thus be labelled as a potential balance for comparing impedance (Z) with change in capacitance (C). The oscillator will give the potential balance when the impedance ratio Z_1/Z_2 is equal, in both magnitude and phase, to the impedance ratio Z_3/Z_4 . The sensitivity of the oscillator-circuit has a direct relationship with the peak height of response curve for a redox system.

Before starting an automatic redox oscillometric titration, the equivalence point of the substrate solution was determined at proper multiplier and sensitivity control knob settings (Figure 1), on the circuit. The total volume of titrant delivered at a constant rate was displayed by the multidisimite (Metrohm, model 655). The reaction solution was stirred at 600 rpm during the entire work. The recorded curves

were of the differential type (Figure 3) with the slope-line segments meeting at the equivalence point. The volume of the titrant used at the equivalence point for a given redox system was computed by the "Tangent Method" [15]. The complete schematic for the auto-redox titrimetric setup is given in Figure 2, which is self-explanatory.

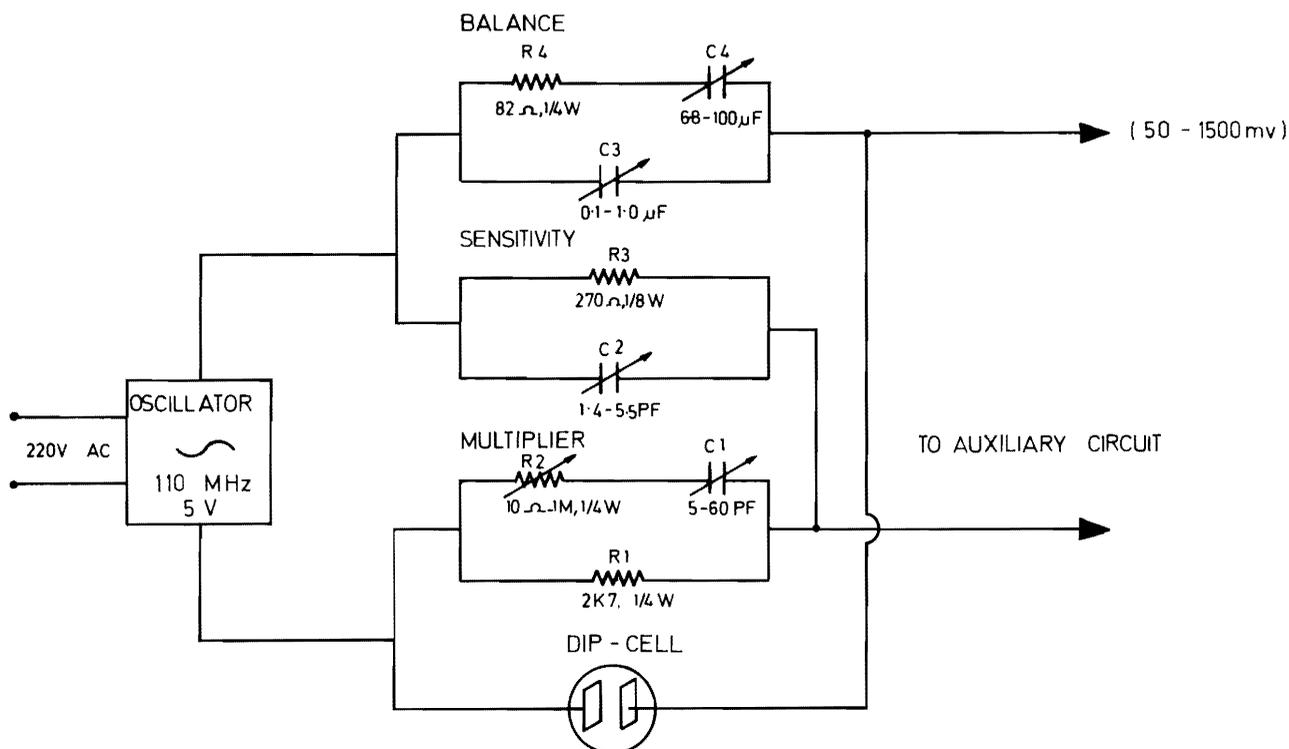


Figure 1. The Circuit Details of the High Frequency Oscillator.

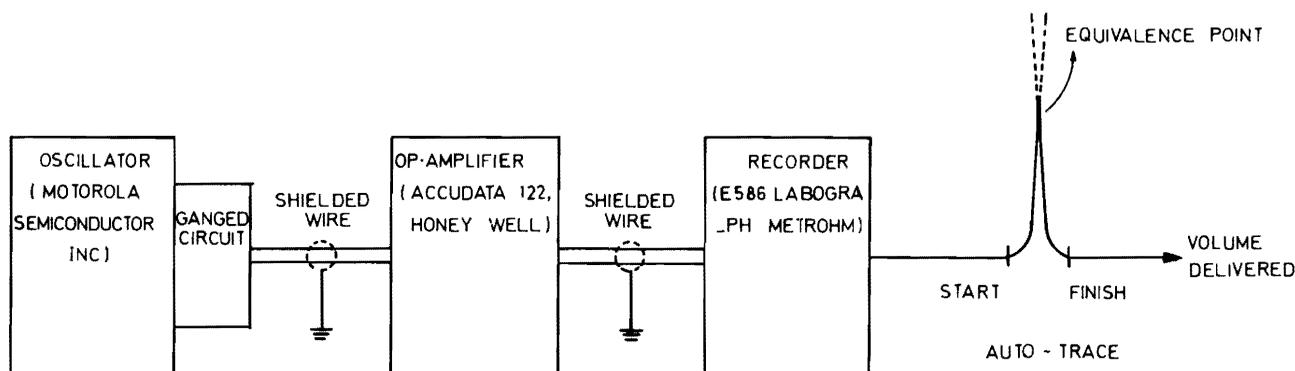


Figure 2. The Schematic Experimental Setup for Autotracing of Redox Titrimetric Events.

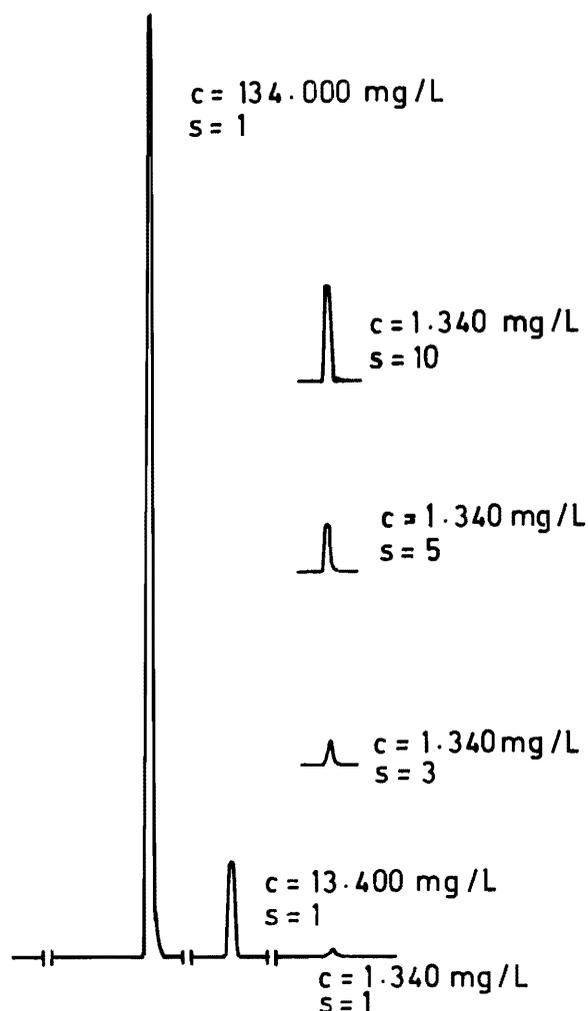


Figure 3. Auto-differential Signals for $\text{KMnO}_4\text{-Na}_2\text{C}_2\text{O}_4$ System Showing Relationship Between Concentration (c) and Sensitivity (s).

DISCUSSION

The proposed technique is based on the phenomenon of polarization, followed by proper amplification of small voltage changes associated with redox-irreversible couples. A constant voltage, when applied to the dip-cell immersed in the solution containing the redox system during the initial reversible redox condition, will flow through the cell which can be recorded after proper amplification directly onto a recorder. The capacitive cell containing the redox system and coupled to the AC oscillator circuit resonating at a frequency of 110 MHz, can monitor changes in the concentration-potential of the chemical system resulting from the addition of the titrant in terms of resistance (impedance). These changes (as a function of time) are amplified as resonant fre-

quency. Any imbalance in response is proportional to the fluctuation in concentration and thus the relevant quantities may be measured by indication of the change in concentration-potential of the redox system. The potential variation thus remains a direct function of concentration changes in a given redox system.

The comparative data on sensitivity (Figure 3) have shown that a 1% change in concentration-potential can easily be recorded. As the sensitivity of the oscillator-circuit has a direct bearing on the peak height, the detection limit could be further enhanced by increasing the gain. Normally, the technique was found to yield results of both high precision and accuracy for samples ranging in concentration as high as 400 mg l^{-1} or as low as 1 mg l^{-1} . The error in the former case was only marginal, but in the case of lower limit of a few mg l^{-1} , the error was relatively higher. This, in fact, is true since most practical data, when derived at high sensitivity level from transformation circuits that become very critical at low concentrations, behave the same way. Basically, the role of the operational differential amplifier is to make the small signals larger (in the direction to increase detection limit) and to perform the function of multiplying the input signal by a constant factor. However, at low concentrations of active species in solution, the upper limit of amplification does not help boost the signal without addition of background noise. If required, the mode of the amplifier may be made flexible to perform the operation of integration, thus permitting a control over the effect of background noise arising at appreciably low concentrations.

A commercial version of an accurately calibrated oscillator (Hewlett-Packard 200 series) and an oscillograph (Du Mont 208) were adopted to operate at 30 MHz in order to validate a comparative study of the data obtained by the present setup. It turned out that the frequency changes attendant on concentration would not be measured satisfactorily with a desirable degree of accuracy. The differential peaks so obtained were both broad and asymmetric and lacked quantitative manipulation. For instance in the case of $\text{KMnO}_4\text{-Na}_2\text{C}_2\text{O}_4$ the error ranged between $\pm 0.60\%$ and $\pm 3.7\%$ for the high and low concentrations, respectively. This almost amounts to a two-fold error in the finished result. The situation was found to be further aggravated with the increase in the sensitivity.

For all redox combinations listed in Table 1, a maximum standard deviation of $\pm 0.5 \times 10^{-4} \text{ M}$ was

Table 1. Comparison of Data on Various Aqueous Phase Redox Substrates^(*).**

Redox System	Actual Concentration (mg l ⁻¹)	Estimated Concentration (mg l ⁻¹)	% Error (±)
KMnO ₄ -FeSO ₄ · 7H ₂ O*	278.000	277.468	0.19
	27.800	27.456	1.24
	2.780	2.723	2.05
KMnO ₄ -Na ₂ C ₂ O ₄ *	134.000	133.619	0.28
	13.400	13.270	0.97
	1.340	1.315	1.87
KMnO ₄ -As ₂ O ₃ *	197.840	197.480	0.18
	19.784	19.578	1.04
	1.978	1.940	1.92
Ce(SO ₄) ₂ -TiCl ₃ *	154.260	153.897	0.23
	15.426	15.269	1.02
	1.543	1.513	1.94
Na ₂ S ₂ O ₃ -KIO ₃ *	126.910	126.630	0.22
	12.691	12.556	1.06
	1.269	1.244	1.97
K ₂ Cr ₂ O ₇ -FeSO ₄	382.160	381.166	0.26
	38.216	37.687	1.38
(NH ₄) ₂ SO ₄ · 6H ₂ O*	3.822	3.737	2.22

**Titrant concentrations ranging between 0.0005 M and 0.005 M

observed between the actual and computed values of concentrations. This corresponded to an average error of about ± 1.1% at the ranges of concentrations estimated. A precision of ± 1% for a given system in triplicate measurements was established. Normally, a flow rate of 4.0 ml min⁻¹ was found adequate for the practical purpose because lower flow rates result in uneven slopes on finished curves leading to obvious problems of quantification. However, the procedure warrants high accuracy within the 10⁻³ to 10⁻⁵ M range. The technique thus has the potential of application for trace estimations in the field of compleximetry and precipitation titrimetry, and for the determination of first and second dissociation constants, the kinetic rate constants and dielectric constants. Further work in these fields is in progress.

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