

## A Differential Amplifier based Autoconductometric Estimation Method for Strong/Weak Acid-Base Systems

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**Summary:** An autoconductometric estimation method is introduced based on the recording of oscillatory current impulses, generated during neutralization events, in an unbalanced Wheatstone bridge coupled to a Wein oscillator. The relevant electronic circuitry and experimental set-up is fabricated from inexpensive, locally available components. The performance of the proposed method is checked on sixteen strong/weak acid-base neutralization systems. The overall average error of the method is rated at  $\pm 1.5\%$  with a precision of  $\pm 0.5\%$  for duplicate measurements. The data are discussed in specific relation to lower detection limit, sensitivity and electrolytic flow rates.

### Introduction

Over the past few years rapid advances in the field of electronics have provided new trends in chemical instrumentation used for various analytical purposes. These advances include basic modification in circuit design, introduction of new operational flexibilities and incorporation of automatic functioning characteristics. Consequently, both reliability and precision attainable in instrumental analysis have gone up in almost every branch of analytical investigation. The field of electrochemistry, in particular, has witnessed the introduction of many such positive innovations. In the area of automatic analytical estimations, the first humble effort was made by Gordon and Cambell [1] who introduced an automatic burette. A modified version was presented later by Farquharson [2] incorporating a digital register in the set-up. Subsequently, Ochme [3], Malmstadt and Hadjiioannon [4], and Grueter [5] introduced similar systems with minor improvements to carry out potentiometric estimation work. In

1963, a differential amplifier was used for the first time for the detection of the end-point of a titration process by Narayanan and Sundararajan [6]. Miyake [7] described an automatic titration apparatus for conventional applications with the titrant added intermittently. Boardman and Warren [8] developed an automatic conductance titrimeter, specifically for work in non-aqueous media. Another conductometric arrangement was described by Holm-Jensen [9] whereby conductivities of electrolytes were graphically recorded by means of commercially available strip-chart, DC potentiometric recorder.

In line with the earlier work, attempt has been made in the present investigation to put forward an automatic conductometric method of general applicability. The proposed method is based, in the first place, upon the development of a simple operational differential amplifier circuit coupled with a Wheatstone Bridge fed by a

Wein oscillatory set-up. The circuitry is very sensitive to high electrolytic impedance in solution media of varied acidic/basic nature. Sixteen acid/base systems are subjected to quantitative test and the data are reported.

### Experimental

The oscillatory circuit was utilized from Beckman Bridge, model RC-16C, in conjunction with the UA741 differential amplifier circuit fabricated from locally available components. The details of the circuit along with component values are given elsewhere [10]. The experimental set-up, and the autoflow regulator used are shown in Figure-1. The flow regulator can be conveniently used to discharge acid/base solutions at any predetermined flow rates ranging from 10.0 ml/min to 30.0 ml/min through the use of a rotating knob that revolves over a precalibrated arbitrary volumetric scale. The flow can be controlled with this device within  $\pm 0.5\%$  of the titrant volume delivered.

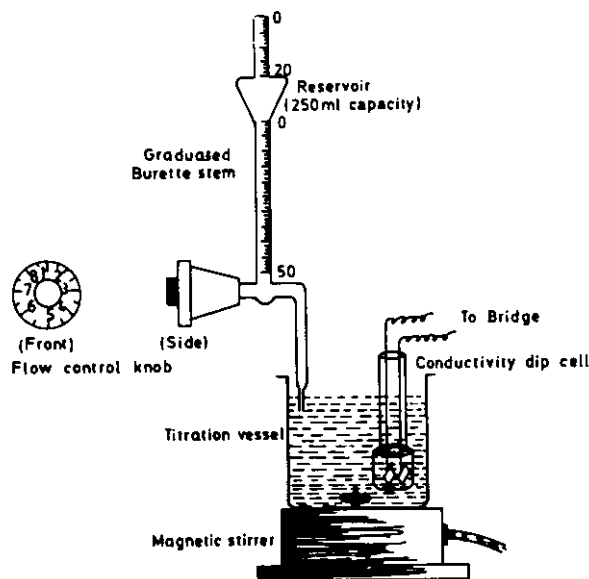


Fig.1: Experimental set-up for autoconductometric estimation

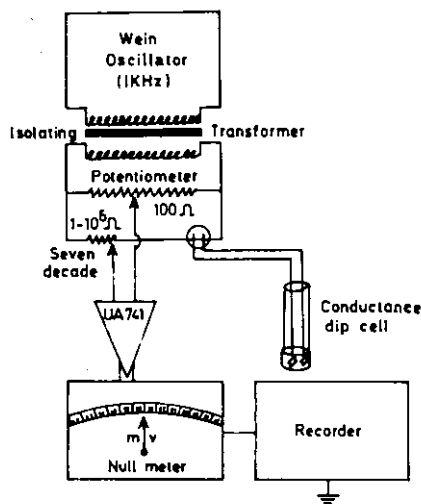


Fig.2: The schematic for obtaining autoconductometric curves

Stock solutions of analytical grade acids and bases at standardized concentrations were prepared in conductivity water. A self explanatory version of the schematic of experimental set-up for the autoconductometric estimation technique is given in Figure-2.

The measuring circuit is an A.C. Wheatstone Bridge powered by a voltage stabilized Wein Bridge oscillator generating 1000 Hz oscillatory electric pulses to minimize any probable polarization problems. The Wein Bridge is a sine wave generator whose frequency is determined by the combined value of resistors and capacitors within its positive feedback loop and its output amplitude determined by an AGC circuit connected within its negative feedback loop. This arrangement allows a range of measurements between  $0.5$  to  $5 \times 10^6$  micro-ohms with an accuracy of  $\pm 1\%$ . The output of the bridge is amplified, rectified and displayed on a null-meter. Any unbalance of the bridge is detected and amplified by the IC operational amplifier.

The experimental procedure involves the titration of a known aliquot of an acid or base, diluted in the reaction vessel to 150.0 ml with conductivity water, against the relevant titrant filled in the flow regulator. After having established a zero potential reading at the null-meter, the titration is started at a predetermined titrant flow rate. As the neutralization event proceeds, the recorder goes on recording the accompanying resistance changes, and hence the concentration changes resulting from the mixing of the two solutions. A typical autocurve so obtained is shown in Figure-3. For locating the equivalence point, the analytical tangent method was selectively found to be more accurate.

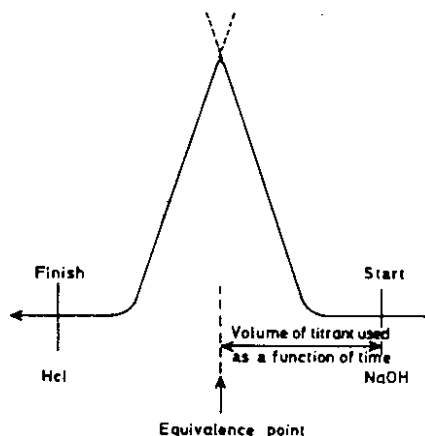


Fig.3: A typical autoconductometric curve for HCl NaOH system.

## Results and Discussion

In Table 1 are listed some of the actual and estimated concentrations of acids and bases selected for the automatic conductometric estimation method. The actual value of concentrations was obtained by direct potentiometric titration in each case. The selection of a particular acid/base combination listed in the table was

rather tentative because the main objective of the present investigation was to check, in the first place, the applicability of the proposed technique on such acid/base systems which differ widely in respect of their dissociation constants. The results obtained by the present technique are, in general, comparably better than those obtained through most careful manual method. The tangential method for obtaining the equivalence point is found to be well applicable to all the combinations listed. The present investigation shows that the combinations that do not differ much in respect of their dissociation constants, give most precise equivalence point. This is specifically true in case of strong acid/base systems. Thus, it turns out that the accuracy of the results obtained is dependent on the nature of the particular acid/base combination chosen for estimation. For strong acid/base system, this technique applies well; while for strong/weak, and weak/weak counterpart systems, it gives auto curves which differ both in slope and configuration. Hence, the quantification of these curves leads to somewhat staggering results. The method gives consistent results upto  $10^{-6}$  M concentration of the individual acid/base systems. Still lower concentration ranges may be covered by incorporating additional capacitance time adjustments. However, the overall accuracy of the technique depends primarily on the accuracy of flow measurement. For very low flow rates, an uneven baseline may be recorded by the recorder. The sensitivity of the bridge circuit has a direct bearing on the peak heights also. By increasing the sensitivity, the peak height may be increased to a desirable limit.

The present technique may be usefully adopted for other areas of conductometric estimations such as

Table-1: Actual vs. estimated concentration of various acid-base systems

S.No.	System	Concentration* (M X 10 <sup>-3</sup> )		% Error
		Actual	Estimated	
1.	HCl-NaOH	1.66	1.63	1.80
2.	H <sub>2</sub> SO <sub>4</sub> -NaOH	1.66	1.63	1.80
3.	HNO <sub>3</sub> -NaOH	1.66	1.63	.180
4.	HNO <sub>3</sub> -NH <sub>4</sub> OH	2.51 1.67	2.54 1.68	1.19 0.59
5.	(COOCH) <sub>2</sub> -NaOH	2.40 3.60	2.36 3.64	1.66 1.11
6.	CH <sub>3</sub> COOH-NaOH	2.40	2.41	0.41
7.	ClCH <sub>2</sub> COOH-NaOH	0.60 2.40	0.59 2.36	1.66 1.66
8.	CH <sub>2</sub> (COOH) <sub>2</sub> -NaOH	2.40 3.60	2.41 3.60	0.41 0.00
9.	(CH <sub>2</sub> COOH) <sub>2</sub> -NaOH	3.60	3.73	3.61
10.	(CH <sub>2</sub> COOH) <sub>2</sub> -NH <sub>4</sub> OH	1.66	1.63	1.80
11.	CH <sub>2</sub> (COOH) <sub>2</sub> -NH <sub>4</sub> OH	2.50	2.56	2.40
12.	CH <sub>3</sub> COOH-NH <sub>4</sub> OH	1.66	1.62	2.40
13.	ClCH <sub>2</sub> COOH-NH <sub>4</sub> OH	2.51 3.34	2.47 3.26	1.59 2.39
14.	HCl-NH <sub>4</sub> OH	1.67 2.51	1.65 2.56	1.19 1.99
15.	H <sub>2</sub> SO <sub>4</sub> -NH <sub>4</sub> OH	1.66 3.34	1.64 3.38	1.20 1.19
16.	(COOH) <sub>2</sub> -NH <sub>4</sub> OH	2.51 3.33	2.55 3.31	1.59 0.60

\* With respect to the base.

complexometry, Redox tritrimetry and the estimation of dissociation constants of acids and bases. In addition, the proposed autoconductometric method provides an excellent means to control many industrial processes involving either the follow-up of the progress of a chemical reaction or the estimation of a varying concentration of an electrolyte. For example, the extent of evaporation of electrolyte solutions, both in aqueous and non-aqueous phase, can be particularly adopted for a continuous operation as a function of time.

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