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Indirect Voltammetric Method for the Determination of Amino Acids Via Charge Transfer Complex Formation Reaction

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Abstract

An easy and sensitive indirect voltammetric method has been proposed for the determination of trace amounts of amino acids, such as proline, glycine, arginine, phenylalanine, glutamic acid, and cysteine, in the range of 50–330 ngmL^{-1} in aqueous solution. It is based on the reaction of chloranil as a π-acceptor with the intended amino acids acting as n-donors, forming an n–π charge transfer complex at pH 9. The reduction peak of (pH 9 – chloranil) solution appears at 0.030 V against the Ag/AgCl. reference electrode. When an aqueous solution of amino acids is added, the peak of solution (pH 9 – chloranil) decreases quantitatively and shifts slightly to 0.024 V. The concentration of amino acids is determined as the current difference decreases. The molar absorptivity ranges between 4.73 ×10^{3} l/mol.cm and 1.82 ×10^{4} l/mol.cm. The accuracy, *i.e.* average recovery ranges from 98.64% to 101.19%, and the precision, *i.e.* relative standard deviation (RSD) is between 0.5% and 9.6%. The limit of detection (LOD) ranges from 1.09×10^{-7} µg/ml to 3.53×10^{-7} µg/mL.

Keywords: Amino acids, Charge transfer complex, Square wave voltammetry

Introduction

Amino acids are organic compounds containing an amino and a carboxylic acid functional group. Foods include free or bound amino acids in proteins, peptides, or nonpeptide-linked polymers. Naturally occurring L-amino acids serve as building blocks for vital compounds, including nucleic acids and coenzymes, and are essential for the creation of proteins. Animal tissues may also include nonprotein amino acids as metabolic intermediates or for other purposes [1]. Amino acids are essential metabolites for tissue metabolism, development, maintenance, and repair [2]. The analysis of amino acids using contemporary analytical techniques has garnered significant attention in recent years due to their multifaceted roles. It is caused by amino acids, which are components of proteins and peptides, being crucial building blocks and precursors for the manufacture of various hormones. Amino acids are essential protein-building ingredients that can also serve as an energy source. Aside from their nutritional function and regulation of gene expression, they play a crucial role in life [3,4]. In analytical chemistry, determining amino acids is a valuable tool in various fields, including food analysis and the qualification of synthetic peptides. There are several methods used for the determination of

amino acids in analytical chemistry, including spectrophotometry [5-8], high-performance liquid chromatography [9-12], thin-layer chromatography [13], electrochemical sensor [14], microwave hydrolysis and UHPLC-MS/MS [15], and voltammetry [16-21]. These methods suffer from limited sensitivity, time-consuming analysis, high cost, and complex sample preparation.

Square-wave voltammetry (SWV) is a second-generation pulse technique in electroanalysis. It is particularly powerful for detecting amino acids because of its high sensitivity and ability to resolve overlapping signals, making it one of the most specific and versatile techniques in the pulse voltammetry family [22-26]. Recently, many researchers have investigated alternative approaches and identified SWV as a promising electrochemical method to overcome the limitations of existing advanced instrumentation [27]. SWV is often used for the direct detection of electroactive amino acids—tyrosine, tryptophan, cysteine, and histidine [28], and can also be applied to non-electroactive amino acids through chemical derivatisation or indirect detection methods [29]. The advantages of the dropping mercury electrode (DME), compared to solid electrodes such as gold, platinum, and glassy carbon, are preferred for the determination of amino acids because its continuously renewable surface prevents fouling caused by adsorbed amino acid molecules. Its high hydrogen overvoltage allows for sensitive detection at more negative potentials [30].

The present method is advantageous due to its sensitivity, requiring only microgram amounts of amino acids for determination. It can be applied to both electroactive and non-electroactive amino acids. Furthermore, it is relatively selective when applied to biological samples, as some substances commonly present in biological fluids do not interfere significantly. The analysis is performed in an aqueous solution, requiring only chloranil reagent and borate buffer. The present method requires no extraction.

Materials and Methods

Chemicals and Reagents

All chemicals used were of the highest purity available and supplied by Fluka, Buchs, Switzerland. Chloranil (1×10^{-3} mol L^{-1}) solution, ethanol (absolute 99-100%), borate buffer of pH 9 and standard solutions of amino acids (1×10^{-5} mol L^{-1}) were used.

Instruments

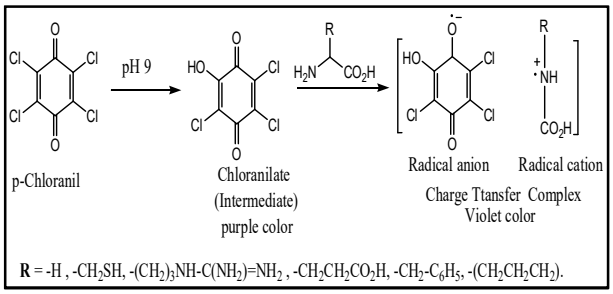
Measurements were taken with an EG and G Princeton Applied Research Model 384B Polarographic Analyzer, a Model 303 A Static Mercury Drop Electrode (GO199 capillary), and a Model RE 0093 Digital Plotter. The setup used a three-electrode system: a hanging mercury working electrode, an Ag/AgCl reference electrode filled with saturated AgCl-KCl solution, and a platinum wire counter electrode. Solutions were heated in a Hakke NK22 water bath, and pH was measured at room temperature using a PW 9421 pH meter. Weighing was performed with an AND Company HR 200 balance.

Recommended Procedure

5 mL of borate pH 9 buffer solution was pipetted into the Model 303 A cell and purged with nitrogen gas for 240 seconds; this blank run was stored in the memory of the analyser. Then 0.9 mL of 1×10^{-3} mol L^{-1} chloranil solution was dispensed into the blank. The sample run was recorded after 30 min. (the time required for the development of maximum peak current), and the sample run was performed according to the instrumental conditions.

Results and Discussion

The reaction of amino acids as n-donors with p-chloranil as a π-acceptor at pH 9, in aqueous medium, results in the formation of charge transfer complexes [31]. This interaction can be represented in Scheme 1.



Scheme 1. **Suggested mechanism for the interaction of p-Chloranil with amino acids.**

Preliminary Investigation

The voltammogram of chloranil (1×10^{-3} mol L^{-1}) has been recorded in the presence of sodium tetraborate (pH 9), which was found to be optimum (Fig. 1). The solution is pipetted into the Model 303 A cell and purged with nitrogen gas for 240 seconds, and a potential range of 0.25 to -0.2 V is applied. Fig. 1A shows the reduction peak of the solution at 0.030 V against the Ag/AgCl reference electrode.

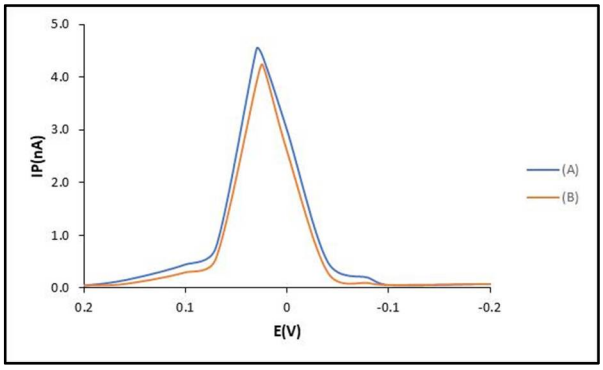


Figure 1. **(A) The reduction peak of only (pH 9 – chloranil) at 0.030 V was 4.54 × 10^4 NA, and (B) the reduction peak after the addition of amino acid at 0.024 V was 4.24 × 10^4 NA**

Upon adding aqueous solution (1×10^{-6} mol L^{-1}) of glycine, a typical amino acid, the peak of (pH 9 – chloranil) decreases quantitatively and shifts slightly to 0.024 V (Fig. 1B).

Study of the Optimum Reaction Conditions

The effect of various parameters on the difference in peak current due to the formation of a charge transfer complex has been investigated (using glycine as a typical amino acid), and the reaction conditions have been optimized.

Effect of Chloranil Solubility

Solutions of chloranil at concentrations of 0.01, 0.001, and 0.0001 mol L^{-1} are prepared in ethanol. Only 0.001 mol L^{-1} gives the highest decrease in current intensity on adding glycine (1.4×10^{-6} mol L^{-1}) (Fig. 2).

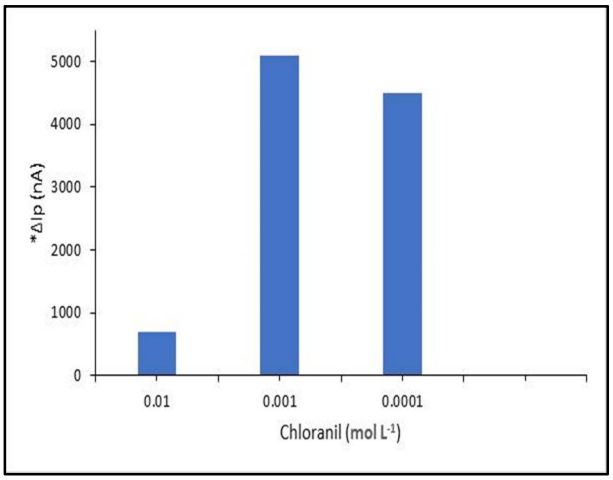


Figure 2. **Effect of chloranil solubility**

Effect of Temperature and Time

The time necessary for the development of the highest peak current of (pH 9 –chloranil) has been investigated at different temperatures up to 50 °C. It was

observed that the peak current shape became distorted and unstable above 30 °C. However, the time required for maximal peak current at room temperature was 30 min, and the peak current was found to remain stable for approximately one hour after that.

After 30 min of adding 5 mL of pH 9 and 1 mL of 1×10^{-3} mol L^{-1} chloranil, glycine was added. It was found that the time required for the maximum decrease in peak current at room temperature was 10 min, and it remained stable for approximately 30 min. An increase in current was observed thereafter (Fig. 3).

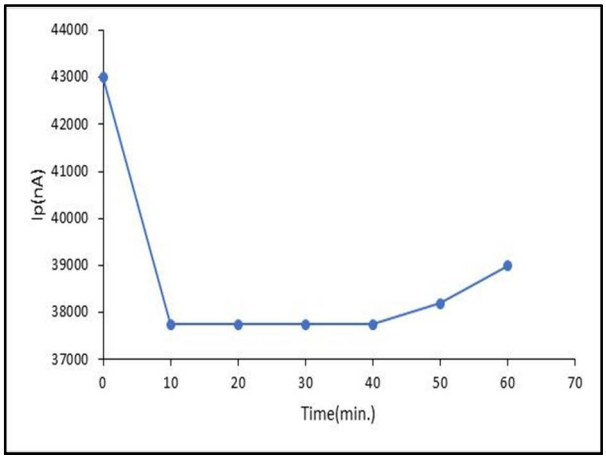


Figure 3. **Time required for the maximum decrease in peak current after the addition of glycine**

Effect of pH

The effect of pH on current intensity is examined using 5 mL of different pH values ranging from 3 to 11 (prepared by various volumes of NaOH and HCl) and keeping the concentration of chloranil constant. Glycine 1 mL of 1×10^{-5} mol L^{-1} was pipetted 30 min after the addition of chloranil solution, and the decrease in current intensity was recorded after 10 min. Fig. 4 shows that the maximum current difference is obtained at pH 9. The same procedure is repeated using different buffers of pH 9, such as phosphate, bicarbonate, borate, and citrate buffers. It was found that the maximum current difference is obtained by using a borate buffer solution, which agrees with the literature [31].

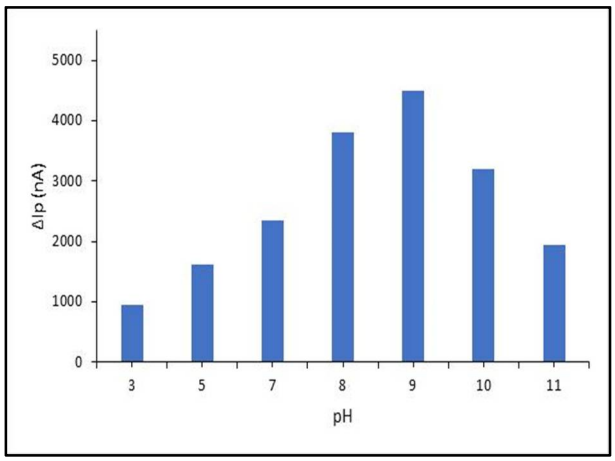


Figure 4. **Effect of pH on current difference**

Effect of Borate Buffer Amount

The effect of the volume of borate buffer solution (pH 9) has been investigated using various volumes (4 to 7 mL) of borate buffer solution, while keeping the concentrations of other components constant. It was found that 5 mL gave the maximum current difference and was used in subsequent experiments.

Effect of Chloranil Reagent Concentration and Volume

Following the procedure used to determine the optimum amount of buffer solution, the amount of chloranil solution required for a pronounced maximum current difference is examined. However, 0.9 mL of 1×10^{-3} mol L^{-1} chloranil solution was found to be optimal.

The same study of optimum reaction conditions as described above was conducted for other amino acids. Only the volume of 1×10^{-3} mol L^{-1} chloranil was found to be changed, Table 1.

Table 1. **Optimum chloranil reagent concentration for amino acids.**

Amino acids	Chloranil (1×10^{-3} mol L^{-1}), (mL)
Glycine	0.9
Arginine	1.0
Phenylalanine	1.0
Glutamic acid	0.9
Cysteine	0.9
Proline	0.5

Optimisation of Instrumental Conditions

The various parameters related to the SWV behaviour of pH 9 – chloranil using 5 mL of pH 9 and 0.9 mL of 1×10^{-3} mol L^{-1} chloranil for the determination of glycine as a module, have been studied, and suitable conditions have been selected.

Effect of Frequency

The effect of frequency on the peak current has been studied. A 120 Hz frequency is selected for the procedure.

Effect of Pulse Height

The effect of pulse height on peak current has been investigated by recording square wave voltammograms of chloranil in a solution containing 5 mL of borate buffer at pH 9 and 0.9 mL of 1×10^{-3} mol L^{-1} chloranil at various pulse heights.

A pulse height of 100 mV has been selected for the subsequent experiments. The peak shape became distorted over 100 mV.

Effect of Deposition Time

A study has been done on the effect of deposition time on peak current. Since there is no influence of increasing the deposition duration on the peak current, 5 seconds were chosen for the next experiments.

Effect of Equilibrium

To verify the effect of equilibrium time on peak height, equilibrium times ranging from 5 to 20 seconds are examined. The results indicate that a 10-second equilibrium time is selected for the subsequent experiments.

Effect of Scan Increment

The effect of scan increment on peak height indicates that a scan increment of 2 mV is the optimum.

However, Table 2 presents the instrumental conditions for determining glycine.

Table 2. **Instrumental conditions for the determination of glycine.**

Initial potential	0.3 V
Final potential	-0.5 V
Frequency	120 Hz
Pulse height	0.1 V
Deposition time	5 second
Equilibrium time	10 second
Scan increment	2 mV
Drop size	Medium
Blank subtraction	No
Tangent fit	No

The same study of instrumental parameters as described above was done for other chloranil concentrations. However, it was found that the optimum instrumental parameters changed only when using 0.5 mL of 1×10^{-3} mol L^{-1} chloranil for the determination of proline, Table 3.

Table 3. **Instrumental conditions for the determination of proline.**

Frequency	80 Hz
Pulse height	100 mV
Deposition time	0
Equilibrium time	0
Scan increment	4 mV

Calibration Graphs and Analytical Results

The calibration graphs for the studied amino acids are plotted under the optimum conditions described above. Table 4 illustrates that the calibration graphs show linear calibration curves that cover the range of 0.05 ppm to 0.33 ppm (3.27×10^{-7} - 2×10^{-6} mol L^{-1}) for amino acids. The concentration coefficient indicates that the method exhibits excellent linearity, with a correlation coefficient≥ 0.9915. The limit of detection (LOD) ranged from 1.09×10^{-7} µg/mL for cystine to 3.53×10^{-7} µg/mL for glutamic acid.

The average recovery percentage ranged between 98.64% for glutamic acid and 101.19% for cysteine, with a relative standard deviation (RSD) of ≤ 9.6% (Table 5).

Table 4. **Linearity ranges, slopes, intercepts, and correlation coefficients for the determination of the studied amino acids.**

Amino acid	Linearity range (mol L^{-1})	Slope	Intercept	LOD (µg/mL)	Correlation coefficient
Glycine	6.34×10^{-7}-1.69×10^{-6}	17367	-9544.8	2.11×10^{-7}	0.9916
Arginine	7.69×10^{-7}-1.43×10^{-6}	8539.8	-5318.2	2.56×10^{-7}	0.9918
Phenylalanine	6.37×10^{-7}-2.00×10^{-6}	10831	-3587.3	2.12×10^{-7}	0.9944
Glutamic acid	1.06×10^{-6}-1.8×10^{-6}	8533.1	-8867.6	3.53×10^{-7}	0.9915
Proline	4.34×10^{-7}-1.54×10^{-6}	18263	-468.18	1.44×10^{-7}	0.9924
Cysteine	3.27×10^{-7}-1.69×10^{-6}	4739.2	-882.18	1.09×10^{-7}	0.9919

Table 5. **Accuracy and precision for the determination of amino acids.**

Amino acid	Amount added (µg/mL)	Average recovery* (%)	RSD* (%)
Glycine	0.048	99.37	8.9
	0.069		2.3
	0.089		0.9
Arginine	0.158	100.36	4.1
	0.205		2.9
	0.227		3.5
Phenylalanine	0.127	100.93	2.5
	0.194		1.1
	0.326		0.7
Glutamic acid	0.195	98.64	8.4
	0.213		3.5
	0.231		1.1
Cysteine	0.099	101.19	9.6
	0.146		3.0
	0.209		1.7
Proline	0.078	100.07	1.2
	0.113		0.8
	0.162		0.5

*Average of six determinations

Methods of Precision and Accuracy

To assess the precision and accuracy of the method, the recovery percentage and relative standard deviation (RSD) for the determination of each amino acid are estimated at three different concentrations. The outcomes displayed in Table 5 indicate reasonably good accuracy (average recovery% is 100.09), while precision (RSD) is in the range between 0.5 and 9.6%.

Interference Study

To assess the selectivity of the suggested method, the interfering effects of various organic and inorganic compounds and other substances that are present in biological samples with amino acids [31] are examined by determining 0.069 µg/mL of glycine (as a typical amino acid) in the presence of each foreign compound using the recommended procedure. The results are shown in Table 6. A relative error of ±5% was considered tolerable in the analysis.

Table 6. **Effect of interference in the determination of 0.069 µg glycine.**

Interferring compound	Fold the excess added	Relative error (%)
	342.0	+ 1
Sodium chloride	413.0	+ 5
	443.0	+ 7
	119.0	+ 3
Citric acid	169.0	+ 4
	235.0	+ 7
	132.0	+ 4
Potassium chloride	157.0	+ 5
	203.0	+ 8
	1.2	+ 1
Disodium hydrogen phosphate	1.6	+ 5
	1.7	+ 6
	1.2	+ 3
Urea	1.7	+ 5
	2.3	+ 9
	1.7	+ 3
Creatine	2.4	+ 5
	3.0	+ 7
	1.7	+ 3
Creatinine	2.1	+ 5
	3.0	+ 15
	1.1	+ 3
Thiourea	1.3	+ 5
	1.7	+ 6
	1.7	+ 3
Ammonium chloride	2.4	+ 4
	3.0	- 7
	132.0	+ 4
Acetamide	169.0	+ 6
	203.0	+ 8
	235.0	+ 4
Sodium bicarbonate	255.0	+ 5
	318.0	+ 8
	132.0	+ 4
Glycerol	169.0	+ 5
	214.0	+ 6
	132.0	+ 3
Xylose	203.0	+ 5
	265.0	+ 6
	145.0	+ 3
Glucose	203.0	+ 4
	255.0	+ 6
	1920.0	+ 4
Acetone	2350.0	+ 5
	2549.0	+ 6

It was found that urea, thiourea, creatine, creatinine, ammonium chloride, and disodium hydrogen phosphate gave positive interferences. Other compounds did not interfere when present in amounts ranging from a 157-fold excess of potassium chloride to a 2350-fold excess of acetone.

Comparison of the Proposed Method with other Literature Methods

The proposed method was compared with other techniques for amino acid determination using square wave measurements as described in the scientific literature. As shown in Table 7, the process is marked by simplicity, speed, and broad estimation ranges. It can be used for all amino acids in aqueous solutions, whether they are electroactive or non-electroactive amino acids, and the resulting product remains relatively stable.

Table 7. **Comparison of the proposed method with published voltammetric methods.**

Parameters	Presentsmethod	Literature method [16]	Literature method [17]	Literature method [18]
Techniques Used	Square Wave Voltammetry (SWV)	Cyclic Voltammetry (CV), Square Wave Anodic Stripping Voltammetry (SWASV)	SWV	SWV
Reaction Type	Charge transfer complex	Complexation reaction: amino acids form complexes with Cu(II) ions in acidic (HCl) or alkaline (NaOH) solution	Derivatization reaction: amino acids reacted with 4-chloro-7-nitrobenzofurazane (CNBD) forming electroactive derivatives	Oxidation via formation of bismuth–cysteinate complex
Reagents	Chloranil	4-chloro-7-nitrobenzofurazane (CNBD, derivatization reagent)	Cu(II) ions (from $CuSO_4$)	Bismuth nanostructure (modifier) - Carbon powder - Ionic liquid (1-octylpyridinium hexafluorophosphate, OPFP)
Temperature	Room temperature (25 ± 1 °C)	Reaction (derivatization): 75 °C, 20 min; Measurements: room temperature (25 °C)	Room temperature (25 ± 1 °C)	Room temperature (25 ± 1 °C)
Target Amino Acids	Glycine Arginine Phenylalanine Glutamic acid Cysteine Proline	Mainly arginine (also applicable to other amino acids after derivatization)	Trp, Ala, Arg, Asp, Lys, Phe, Tyr, Asn	Cysteine (Cys) (thiol amino acid)
Linearity Range (mol L^{-1})	3.27×10^{-7} - 2×10^{-6} mol L^{-1}	2.0×10^{-8} – 1.0×10^{-6} mol L^{-1} for Arg–CNBD complex (SWV)	5.0×10^{-6} – 2.0×10^{-4} mol L^{-1} for amino acids (Cu-complexation, SWV)	1.0×10^{-6} – 2.0×10^{-3} mol L^{-1}
Interferences	urea, thiourea, creatine, creatinine, ammonium chloride, and disodium hydrogen phosphate gave positive interferences	Minimal interference from other amino acids (due to selective CNBD derivatization); but some overlap with lysine reported	Interference from Cu-binding amino acids	Thiol compounds interfere
Medium	Aqueous	organic methanol (derivatization)	Aqueous	Aqueous
Buffer	Borate	(phosphate, acetate, borate) Buffers	acidic (HCl) and alkaline (NaOH)	Acetate buffer
pH Values Studied	pH 9.0	pH 2.0 (phosphate buffer)	pH ≈1 (HCl) and pH ≈13 (NaOH)	pH 4.5
Average Recovery (%)	Average recovery% is 100.09	~95–105% (RSD 2–6%) depending on amino acid	79 ± 3% for amino acids in urine	97.3 – 106.3%
RSD (%)	Range between 0.5 and 9.6%.	2–6% depending on amino acid (n = 5)	< 5.7% (arg), < 6.2% (other amino acids)	2.3%

Conclusion

A sensitive indirect voltammetric method has been proposed for determining amino acids in aqueous solution. It is based on the reaction of chloranil as a π-acceptor with the intended amino acids as n-donors, forming an n-π charge transfer complex at pH 9. Following the decrease in the current intensity of unconsumed chloranil, the current difference is a measure of amino acid concentration.

According to the research results, the technique is simple, sensitive (molar absorptivity ranging from 4.73×10^3 to 1.82×10^4 l/mol·cm for the applied amino acids), and accurate (average recovery is 100.09%), while precision (RSD) ranges between 0.5 and 9.6%. The method shows good applicability and was successfully used for the determination of both electroactive and non-electroactive amino acids. .

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Conflict of Interest

The authors declare no conflict of interest.

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