## 9. Output จากโครงการวิจัยที่ได้รับทุนจาก สกว.

1. ผลงานวิจัยที่ตีพิมพ์ในวารสารวิชาการระดับนานาชาติ

   (1) J. Jakmunee and K. Grudpan, Flow Injection Amperometry for the Determination of Iodate in Iodized Table Salt, Anal. Chim. Acta, 438 (2001) 299-304.

   (2) J. Jakmunee, S. Suteerapataranon, Y. Vaneesorn and K. Grudpan, Determination of Cadmium, Copper, Lead and Zinc by Flow Voltammetric Analysis, Anal. Sci., submitted.

2. การนำผลงานวิจัยไปใช้ประโยชน์

1) ระบบ on-line voltammetry สำหรับการวิเคราะห์ Zn, Cd, Pb และ Cu ได้นำมาใช้ในการบริการตรวจวิเคราะห์ตัวอย่างน้ำของสถานบริการวิทยาศาสตร์และเทคโนโลยี คณะวิทยาศาสตร์ มหาวิทยาลัยเชียงใหม่

2) เครื่องโวลแทมโมกราฟอย่างง่ายที่สร้างขึ้นได้นำมาใช้ในการเรียนการสอนของภาควิชาเคมี

3) งานวิจัยตามโครงการนี้มีส่วนสนับสนุนการทำวิทยานิพนธ์ของนักศึกษาปริญญาเอก 3 คน และนักศึกษาปริญญาโท 2 คน และการทำวิจัยปัญหาพิเศษของนักศึกษาปริญญาตรี 6 คน

3. อื่น ๆ (เช่น ผลงานตีพิมพ์ในวารสารวิชาการในประเทศ การเสนอผลงานในที่ประชุมวิชาการ หนังสือ การจดสิทธิบัตร)

ได้นำเสนอผลงานในการประชุมวิชาการระดับนานาชาติ "8th International Conference on Flow Analysis" ซึ่งจัด ณ กรุงวอร์ซอร์ ประเทศโปแลนด์ระหว่างวันที่ 25-30 มิ.ย. 2543 ซึ่งได้เสนอผลงานวิจัยที่เกี่ยวข้องกับโครงการนี้ และโครงการอื่น ๆ รวม 5 เรื่องดังนี้

1. Flow Injection Amperometry for Determination of Iodate in Iodized Table (โครงการนี้)

2. Sequential Injection Systems for the Determination of Ascorbic Acid or Acetic Acid
3. Determination of Trace Iron by Reverse Flow Injection with Chemiluminescence Detection
4. Flow Injection Dialysis with Ion-Chromatography
5. Determination of Ethanol in Liquor by Near-Infrared Spectrophotometry with Flow Injection

ได้นำเสนอผลงานในการประชุมวิชาการระดับนานาชาติ "IUPAC International Congress on Analytical Science 2001 (ICAS2001)" ซึ่งจัด ณ กรุงโตเกียว ประเทศญี่ปุ่นระหว่างวันที่ 6-10 ส.ค. 2544 ซึ่งได้เสนอผลงานวิจัยที่เกี่ยวข้องกับโครงการนี้ และโครงการอื่น ๆ รวม 5 เรื่องดังนี้

1. Determination of Cadmium, Copper, Lead and Zinc by Flow Voltammetric Analysis (โครงการนี้)
2. Flow Injection Sample Pretreatment for Determination of Lead by Flame Atomic Absorption Spectrophotometry
3. A Simple Semiautomatic Stopped Flow Injection Analyzer: A Performance Test for Phosphate Determination
4. Combination of Field flow Fractionation with Flow Injection Analysis
5. A Cost-Effective Gravitational Field-Flow Fractionation System

ได้เสนอผลงานในการประชุมวิชาการระดับชาติ คือ การประชุมวิชาการวิทยาศาสตร์และเทคโนโลยีแห่งประเทศไทย (วทท.) ครั้งที่ 25 (19-21 ตุลาคม 2542, พิษณุโลก) ครั้งที่ 26 (18-20 ตุลาคม 2543 และครั้งที่ 27 (16-18 ตุลาคม 2544, สงขลา) ดังนี้

1. Flow injection amperometry for determination of iodate in iodine added table salt เสนอใน วทท. 25
2. On-line voltammetric system for metals determination in water เสนอใน วทท. 26
3. Voltammetric determination of fumaric acid in fruit juice เสนอใน วทท. 26
4. Fabrication and performance test of a simple voltammograph for teaching เสนอใน วทท. 27
5. Study of the electrochemical reactions of iodate iodide and iodine by cyclic voltammetry เสนอใน วทท. 27
6. Efficiency in reducing of arsenate to arsenite by sodium thiosulphate เสนอใน วทท. 27

งานวิจัยนี้ยังมีส่วนเสริมในโครงการอื่น ๆ ซึ่งสามารถตีพิมพ์งานวิจัยในวารสารนานาชาติ และการเสนอผลงานในการประชุมวิชาการต่าง ๆ ได้แก่

1. Flow injection spectrophotometric speciation of Cr(VI) and Cr(III) using diphenylcarbazide and solid phase extraction with C18 in-valve mini-column, Science Asia, 25 (1999) 99-106.
2. Cost Effective Flow Injection Dialysis Systems for Acetic Acid, Lab Robotics and Automation, 12 (2000) 129.
3. Automated Monitoring System for Quality of Treated Wastewater from a Power Plant by Incorporating Flow Injection Analysis, Lab Robotics and Automation, 12 (2000) 164.
4. Determination of Ethanol in Liquor by Near Infrared Spectrophotometry with Flow Injection, Talanta, 53 (2001) 1199.

5. Flow injection potentiometry for chloride determination เสนอใน วทท. 25
6. Simple Automatic Titration System for Teaching เสนอใน วทท. 25
7. Determination of some anions in water samples by flow injection dialysis- ion chromatography เสนอใน วทท. 25
8. Determination of titanium(IV) by on-line dilution flow injection spectrophotometry เสนอใน วทท. 25
9. Performance test for a simple field flow fractionation system เสนอใน วทท. 25
10. Spectrophotometric determination of iodine number for edible oil เสนอใน วทท. 25
11. Simple gravitational field-flow fractionation for silica gel 60 G (5-20 microns) เสนอใน วทท. 26
12. Development of high performance liquid chromatography for the determination of iodide at tracelevels เสนอใน วทท. 26
13. A study on the leachiang of some metals from tin tailings เสนอใน วทท. 26
14. Determination of diphenhydramine hydrochloride in pharmaceutical preparations by flow injection spectrophotometry เสนอใน วทท. 26
15. On-line dilution flow injection system using potassium permanganate reagent for determination of ascorbic acid in pharmaceutical preparations เสนอใน วทท. 26
16. Development of flow injection spectrophotometry for determination of ascorbic acid in fruit juices using 2,6- dichlorophenol indophenol with on-line dialysis เสนอใน วทท. 26
17. Flow Injection Determination of trace iron by using Packard Radiometric FLOONE®\Beta series A-100 as a chemiluminescence detector เสนอใน วทท. 26

18. Development of sequential injection analysis for acidity in fruit juice เสนอใน วทท. 26
19. Speciation of Fe(II)/Fe(III) using flow injection spectrophotometry with 1,10-phenanthroline เสนอใน วทท. 26

# ภาคผนวก ก

Flow Injection Amperometry for the Determination of Iodate in Iodized Table Salt, Anal. Chim. Acta, 438 (2001) 299-304.

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# Flow injection amperometry for the determination of iodate in iodized table salt[☆]

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**Abstract**

A very simple flow injection amperometric system for determination of iodate has been developed. Cyclic voltammetry was used to study reactions of iodate, iodide and iodine on a glassy carbon electrode. A single line manifold of the flow system consists of a pulse-free reagent propulsion using a simple Mariotte bottle, a home-made injection valve, and a cross flow electrochemical cell with a potentiostat for control a potential of glassy carbon working electrode at +200 mV versus Ag/AgCl electrode. Using a solution of 1.0% w/v NaCl, 0.02% w/v KI and 0.1 M HCl as a reagent and a flow rate of 2 ml/min, a linear calibration up to 25 mg/l $IO_3^-$ with a detection limit of 0.5 mg/l $IO_3^-$ was obtained. Relative standard deviation for 10 injections of 10 mg/l $IO_3^-$ solution was 1.7%. A sample throughput of 35 injections per hour was achieved. The system was successfully applied for determination of iodate in iodized table salts, validating by the AOAC titrimetric method.

*Keywords:* Iodate; Flow injection analysis; Amperometry; Voltammetry; Iodized salt

## 1. Introduction

Iodine is an essential micronutrient, which is an essential part of the thyroid hormones that play an important role in the development of brain function and cell growth. Deficiency of iodine can result in a serious delay in neurologic development. Otherwise, an excess of iodine or iodide can produce goitre and hypothyroidism as well as hyperthyroidism [1]. Iodine is absorbed from foods, drugs and water. Iodate is added to an iodized table salts as a source of iodine for preventing of iodine deficiency disorders in population of Thailand [2].

Several techniques have been applied for the determination of iodate. The spectrophotometry utilizing the reaction of iodate with excess iodide to form triiodide which absorbs strongly at about 350 nm is widely used [3,4]. Other spectrophotometric methods employ the oxidation of iodate to periodate which was forming a suitable ion-pair compounds and extracted into organic solvent before detection [5,6]. Iodate and other halogen anions were determined by ion chromatography with spectrophotometry [7,8] or mass spectrometry [9,10] detection. Trace amounts of iodine, iodide and iodate in drinking water were determined by gas chromatography–mass spectrometry after pre-derivatization into 4-iodo-2,6-dimethylphenol and extracted with diethyl ether [11]. Chemiluminescence

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determination of iodate was based on the reaction with excess of iodide in acidic solution, gas extraction of the iodine formed and detection in the stream of carrier gas by alkaline luminol solution [12]. Flow injection amperometric determination of iodate was made by electroreduction of iodate at a molybdenum oxide modified electrode [13].

In this work, we developed a very simple flow injection amperometric system for the determination iodate using a Mariotte bottle as a solution propulsion device. The iodate reacts with excess iodide in acidic medium to produce iodine which is subsequently reduced at a glassy carbon electrode. The reactions of iodate, iodide and iodine at GCE were studied by cyclic voltammetry. The proposed method was applied for iodized table salts.

## 2. Experimental

### 2.1. Chemicals

All chemicals used were of analytical-reagent grade and deionized water was used throughout. An iodate standard stock solution (1000 mg/l) was made by using $KIO_3$ (BDH, Poole, UK). The working standard solutions were obtained by dilution of the stock solution with deionized water. Sodium chloride (Merck, Darmstadt, Germany) and hydrochloric acid (Merck, Darmstadt, Germany) were used to prepare an electrolyte solution for voltammetric studies. Reagent for flow injection amperometry was made by dissolving NaCl and KI (Merck, Darmstadt, Germany) in 0.1 M HCl.

### 2.2. Instrumentation

A computerized voltammetric analyzer BAS CV-50W (Bioanalytical System (BAS), IN, USA) was used for all voltammetric and amperometric experiments. A C2 cell stand (BAS, IN, USA) comprising a glassy carbon disc electrode (GCE) of 3 mm diameter as a working electrode, a platinum wire auxiliary electrode and a Ag/AgCl reference electrode was used for cyclic voltammetric studies.

Flow injection system was constructed using a simple home-made Mariotte bottle as a solution propulsion device, a home-made injection valve [14] and a cross flow electrochemical cell, MF-2400 (BAS, IN, USA) consisting of a glassy carbon cross flow working electrode (5 mm diameter), an auxiliary electrode (stainless steel flow cell body) and a Ag/AgCl reference electrode (see Fig. 1(b)).

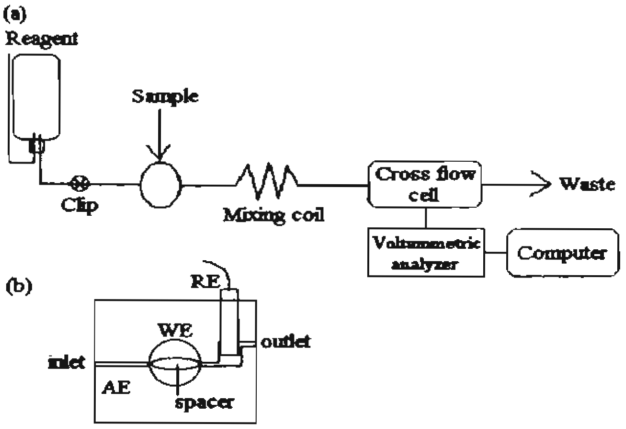

Fig. 1. Flow injection amperometric system for iodate: (a) manifold and (b) cross flow cell diagram (AE: auxiliary electrode, WE: working electrode, RE: reference electrode).

### 2.3. Flow injection manifold

The diagram of flow injection amperometry is depicted in Fig. 1. A reagent solution consisting of 1.0% w/v NaCl, 0.02% w/v KI and 0.1 M HCl was put in a home-made Mariotte bottle which was built from an empty drinking water bottle. The bottle provided a pulse-free constant flow rate of a solution at 2 ml/min. A standard or sample solution was injected into the system via a home-made two-loop injection valve [14]. The iodate reacts with iodide in acidic medium producing iodine which further reduces to iodide at a GCE working electrode with a potential of +200 mV versus Ag/AgCl. The reduction current was monitored by a voltammetric analyzer and recorded by a software of the instrument.

### 2.4. Determination of iodate in iodized table salt

Iodized table salt samples were purchased from local market. A sample was weighed and dissolved with deionized water. Each resulted solution was analyzed by the above flow injection amperometric system, a flow injection spectrophotometric method [15] and a titrimetric method [16].

## 3. Results and discussion

### *3.1. Study of the reaction of iodate iodide and iodine at electrode by cyclic voltammetry*

Cyclic voltammetry was used to study the reaction of iodate, iodide and iodine (convert from iodate by addition of excess iodide) on GCE in 1.0% (w/v) NaCl and 0.1 M HCl electrolyte solution. The potential of GCE (versus Ag/AgCl) was scanned from +1000 to 0 mV and then back to +1000 mV, with a scan rate of 100 mV/s in both direction. The voltammograms obtained are shown in Fig. 2. It indicates that reduction of iodate takes place at a potential more negative than +200 mV. Iodide has an oxidation peak potential at +584 mV. Reduction of iodine occurs at peak potential of +270 mV, with higher peak current than that of the iodate reduction. Potential of the GCE was fixed at +200 mV for amperometric monitoring in the flow injection system which no reaction of either iodate or iodide takes place. Due to no interfering from oxygen, it is then not necessary to degas the solution.

### *3.2. Solution propulsion device*

A home-made Mariotte bottle assembled by using an empty drinking water bottle was used as a solution propulsion device. An air inlet and a solution outlet tubings were inserted on a bottle cap. The liquid discharge rate from the Mariotte bottle remains constant until the fluid level drops below the air inlet tube [17]. The flow rate is dependent on a cross section area of a solution outlet tube, which can be adjusted by a restriction clip placing on a flexible outlet tube. The bottle provided a pulse-free constant flow rate of a solution at about 2 ml/min for at least 350 min as depicted in Fig. 3. The reagent solution should be filtered before use in order to get rid of particles that may block the aperture of the outlet tube and may lead to change in flow rate.

### *3.3. Optimization of flow injection amperometric system*

A multi-variation procedure was applied for parameters optimization. A series of iodate standard solutions (0–25 mg/l $IO_3^-$) or a 25 mg/l $IO_3^-$ solution was injected into the system. By considering for a higher value of either a slope of a calibration graph or of a blank corrected peak height of 25 mg/l $IO_3^-$ solution,

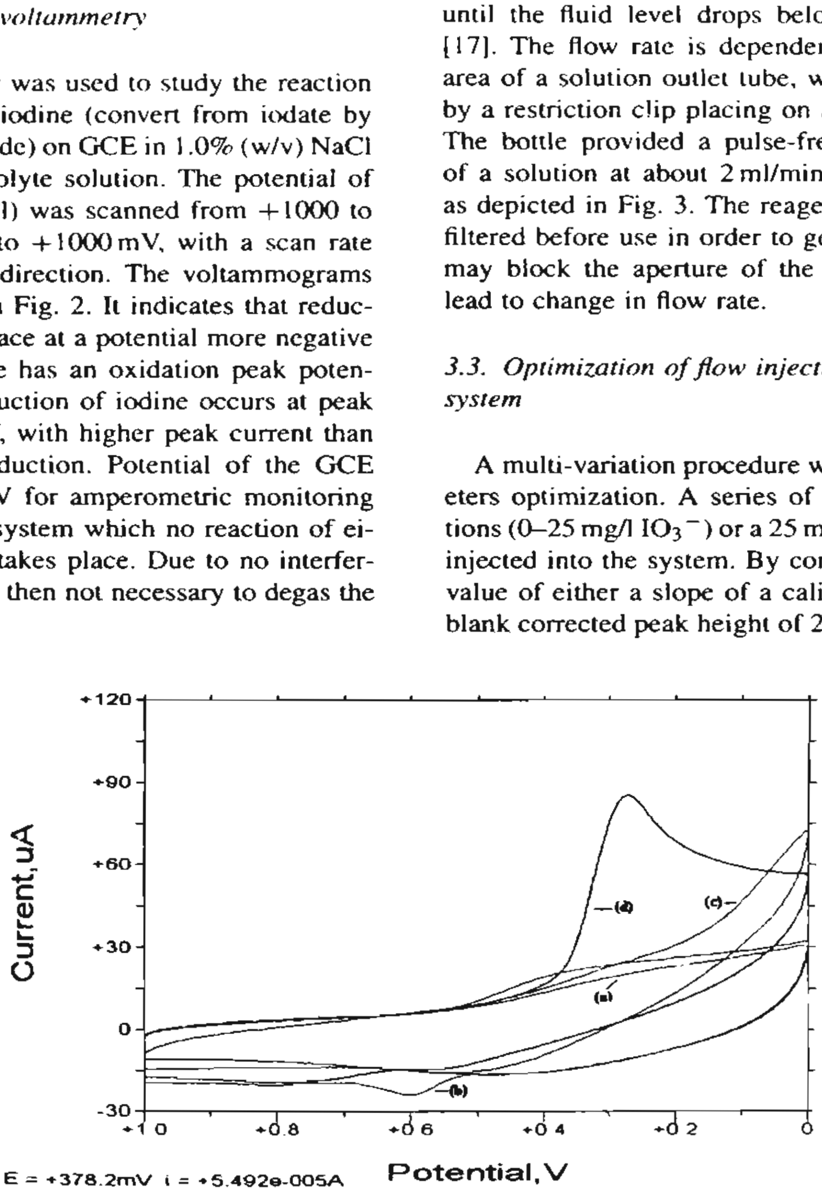

Fig. 2. Cyclic voltammograms of (a) electrolyte (1.0% w/v NaCl and 0.1 M HCl), (b) 0.01% w/v KI, (c) 100 mg/l $IO_3^-$, and (d) 0.01% w/v KI and 100 mg/l $IO_3^-$ in electrolyte solution (initial potential (init $E$) = +1000 mV, high $E$ = +1000 mV, low $E$ = 0 mV, scan rate = 100 mV/s, scan direction: negative, sensitivity = 100 μA/V).

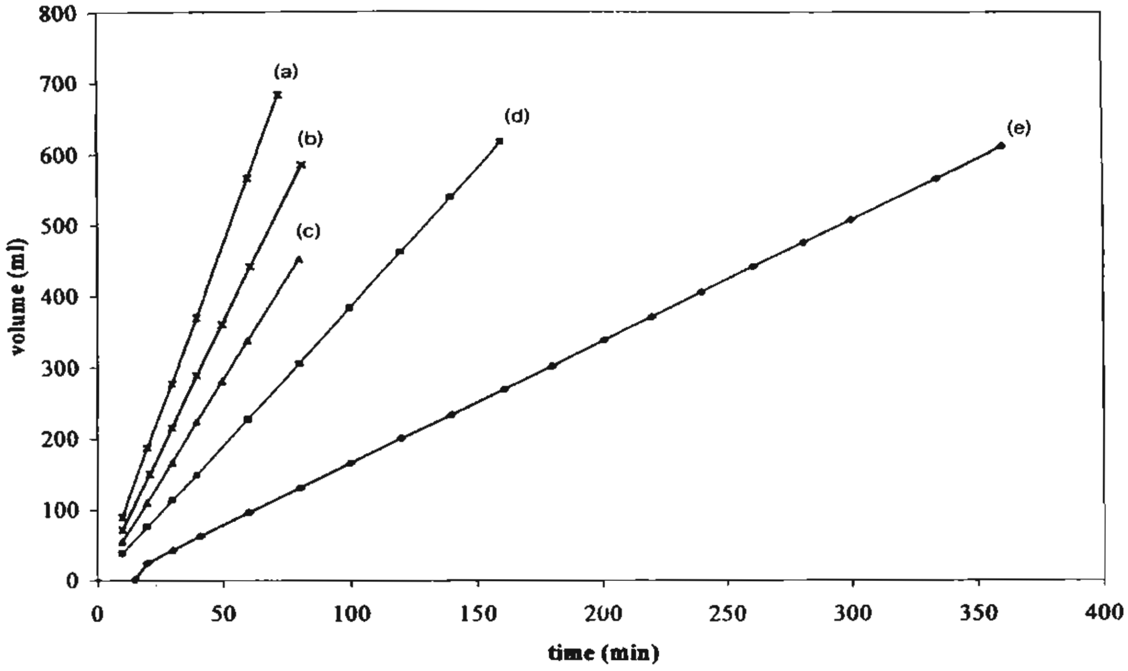

Fig. 3. Discharge of water from a Mariotte bottle with a flow rate of (a) 9.6; (b) 7.2; (c) 5.6; (d) 3.8 and (e) 1.7 ml/min (the values obtained from the slopes).

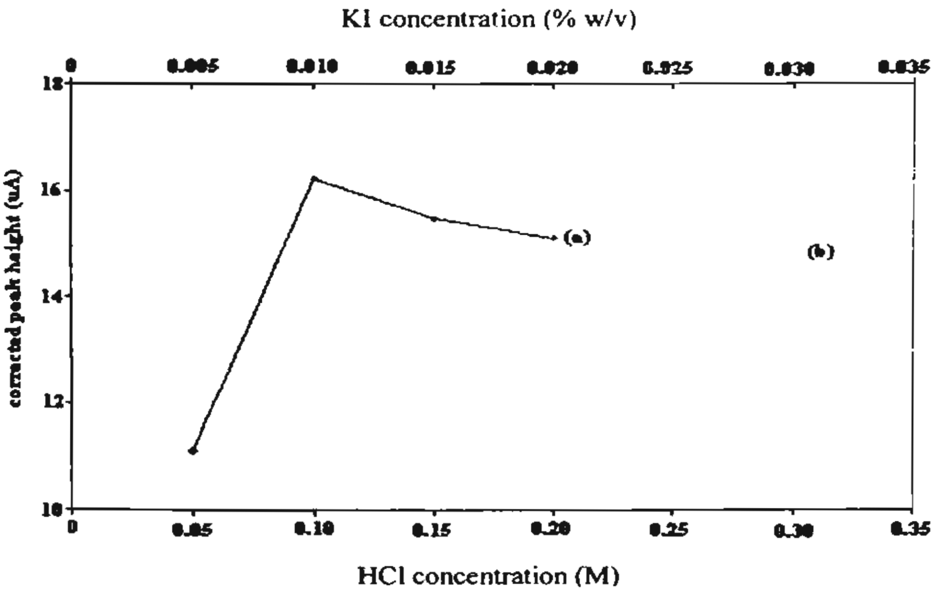

Fig. 4. Effect of (a) HCl and (b) KI concentration in the carrier solution on blank corrected peak height of 25 mg/l $IO_3^-$.

Table 1
Optimum condition of the flow injection amperometric system for iodate

| Parameter | Condition | |
|---|---|---|
| | Studied range | Optimum |
| KI concentration (% w/v) | 0.005–0.030 | 0.020 |
| NaCl concentration (% w/v) | 0.1–10.0 | 1.0 |
| HCl concentration (M) | 0.05–0.20 | 0.10 |
| Flow rate (ml/min) | 0.5–5 | 2 |
| Sample volume (μl) | 50–150 | 100 |
| Mixing coil length (cm) | 0–200 | 100 |
| Measurement mode[a] | – | Time base |
| Electrode[a] | – | GCE 3 mm diameter |
| Electrode potential[a] | – | +200 mV versus Ag/AgCl |
| Sensitivity (μA/V)[a] | – | 10 |

[a] Voltammetric analyzer.

condition for each parameter was selected. Effect of hydrochloric acid and potassium iodide concentrations in the reagent solutions represented in Fig. 4. The studied range and optimum conditions are summarized in Table 1.

### 3.4. Calibration and determination of iodate in iodized salts

Using the optimum conditions, a series of iodate standard solutions of different concentrations (0, 5, 10, 15, 20 and 25 mg/l $IO_3^-$) were injected into the system. A linear calibration graph obtained represents by an equation $y = 1.42x + 2.63$; correlation coefficient $r = 0.995$, where $y$ and $x$ are peak height (μA) and iodate concentration (mg/l), respectively. The detection limit ($3\sigma$) was 0.5 mg/l $IO_3^-$ and relative standard deviation was 1.7% for 10 replicate injections of 10 mg/l $IO_3^-$ standard solution. A sample solution was injected under the same condition as that of the standards. An iodate concentration was calculated from a calibration equation using the peak height obtained. The results obtained by the proposed method agree well with the ones obtained from flow injection spectrophotometric method [15] and AOAC titrimetric method [16] as summarized in Table 2. It should be noted that the results obtained by the three methods exhibit no trends in correlation to each other. This could be due to the inhomogeneity in a solid sample. A $t$-test was performed at 95% confidence level [18]. Calculated $t$-values for the results obtained by flow injection amperometry versus the ones by flow injection spectrophotometry and versus the ones by titration are 0.661 and 0.504, respectively, while the value in table is 2.365 for d.f. of 7.

Table 2
Iodate found in iodized table salt samples by different methods

| Sample | Iodate found by different methods (mg/kg)[a] | | |
|---|---|---|---|
| | FI-amp | FI-spec | Titration |
| 1 | 64.9 (1.7)[b] | 66.4 (0.3) | 76.0 (1.6) |
| 2 | 50.6 (1.4) | 48.5 (0.8) | 54.0 (0.8) |
| 3 | 42.7 (1.7) | 35.1 (0.0) | 36.5 (1.3) |
| 4 | 50.4 (1.0) | 64.5 (0.0) | 53.7 (1.0) |
| 5 | 52.6 (0.2) | 51.5 (0.7) | 54.7 (0.0) |
| 6 | 70.7 (3.0) | 63.5 (0.3) | 69.6 (0.1) |
| 7 | 98.3 (1.7) | 93.6 (0.8) | 101.7 (0.6) |
| 8 | 214.4 (3.1) | 208.2 (0.2) | 206.9 (0.1) |

[a] FI-amp: flow injection amperometry; FI-spec: flow injection spectrophotometry.

[b] Values in parentheses are relative standard deviations.

## 4. Conclusion

A very simple flow injection amperometric system with a simple solution propulsion device based on the principle of a Mariotte bottle for the determination iodate is developed. The method utilized the reaction of iodate with excess iodide in acidic medium to produce iodine which is subsequently can be reduced at a GCE, so no complex modified electrode is required. The reactions of iodate, iodide and iodine on a GCE or platinum electrode were studied by cyclic voltammetry. The proposed method was successfully applied to iodized table salts.

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# ภาคผนวก ข

Simple automatic titration system for teaching

ผู้อธิบายงานวิจัย นพวรรณ ศรีโพธิ์

■ น.ส. ☐ นาง ☐ ดร. ☐ อ. ☐ ผศ. ☐ รศ. ☐ ศ.

ภาควิชาเคมี คณะวิทยาศาสตร์ มหาวิทยาศาสตร์
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■ วิทย์-ศึกษา ☐ ทั่วไป

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# Simple Automatic Titration System for Teaching *

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A simple automatic titration system was developed. A " mariotte bottle" was used as a device for providing a constant rate delivery titrant. The titration system for acid-base was constructed utilising a pH-meter for detection and a recorder for titration curve plotting. The system shortens an analysis time and provides more important informations. It can be used for teaching a analytical chemistry laboratory course, in comparison with manual titration that using an indicator for end point detection.

A research supported by Chiang Mai University

# ระบบไตเตรชันอย่างง่ายสำหรับการเรียนการสอน *

จรูญ จักร์มุณี นพวรรณ ศรีโพธิ์ และ อิสระ ศรีตระกูล
ภาควิชาเคมี คณะวิทยาศาสตร์ มหาวิทยาลัยเชียงใหม่ อ. เมือง จ. เชียงใหม่ 50200

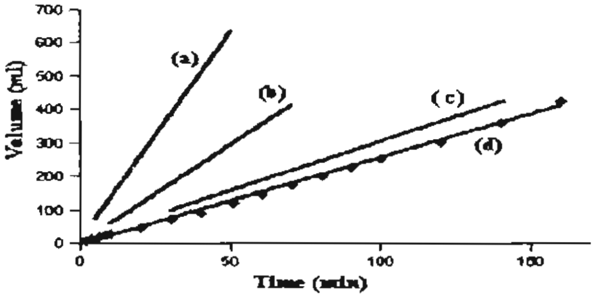
ได้พัฒนาระบบไตเตรชันอัตโนมัติอย่างง่ายขึ้น โดยใช้" mariotte bottle" เป็นอุปกรณ์ในการจ่ายไตรเตรนต์ด้วยอัตราคงที่ ได้สร้างระบบในการไตเตรต กรด-เบส โดยใช้พีเอชมิเตอร์เป็นเครื่องตรวจวัดและบันทึกกราฟการไตเตรตด้วยเครื่องบันทึกสัญญาณ ทำให้ได้ผลการวิเคราะห์ในเวลาอันสั้น และให้ข้อมูลที่สำคัญมากขึ้น ระบบที่พัฒนาขึ้นนี้สามารถประยุกต์ในการเรียนการสอนวิชาปฏิบัติการเคมีวิเคราะห์ โดยการเปรียบเทียบกับการไตรเตรตธรรมดาที่ใช้อินดิเคเตอร์ชี้บอกจุดยุติ

* งานวิจัยนี้ได้รับการสนับสนุนจากมหาวิทยาลัยเชียงใหม่

INDEX KEY WORDS: Automatic titration,acid-base,teaching

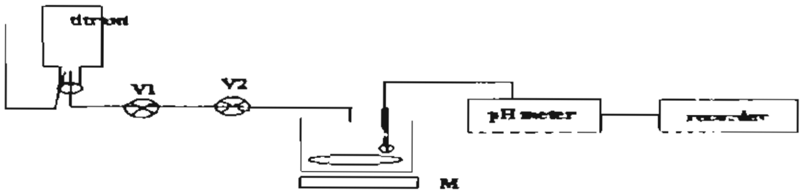
ชื่อเรื่อง (ไทย) **ระบบไตเตรชันอย่างง่ายสำหรับการเรียนการสอน**

การพัฒนาระบบไตเตรชันอัตโนมัติเกี่ยวข้องกับ 4 ส่วนสำคัญคือ ระบบจ่ายไตเตรนต์ ระบบตรวจวัด ระบบบันทึก และระบบควบคุม[1] ในที่นี้ได้ศึกษาระบบจ่ายไตเตรนต์ที่ใช้หลักการของ "mariotte bottle" [2] ได้ผลดังรูป 1

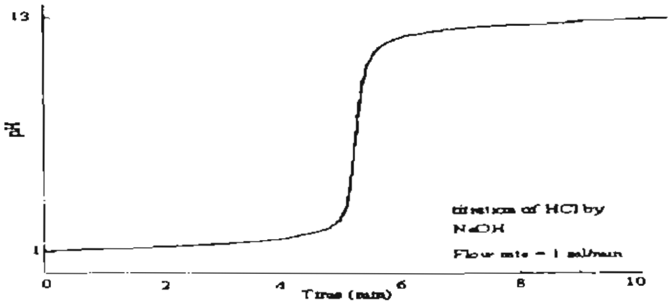


รูป 1 ปริมาตรของไตเตรนต์ที่เวลาต่าง ๆ เมื่อจ่ายด้วย flow rate (a) 12.5 (b) 5.9 (c) 3.0 และ (d) 2.6 ml $\text{min}^{-1}$

ระบบไตเตรชันที่สร้างขึ้นแสดงดังรูป 2 ซึ่งได้ประยุกต์ในการไตเตรต กรด-เบส สามารถบันทึก titration curve ได้ดังรูป 3



รูป 2 แสดงส่วนประกอบของระบบ Automation titration ที่สร้างขึ้น V1 = open/close valve, V2 = flow rate control valve, M= Magnetic stirrer



รูป 3 titration curve ที่ได้จากการใช้ระบบในรูป 2

**เอกสารอ้างอิง**

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# ภาคผนวก ค

Determination of Cadmium, Copper, Lead and Zinc by Flow Voltammetric Analysis, Anal. Sci., submitted.

# etermination of Cadmium, Copper, Lead and Zinc by Flow oltammetric Analysis

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Abstract: Flow analysis with voltammetric system for determination of cadmium, copper, lead and zinc has been developed. Mercury film working electrode (MFE) was prepared by on-line mercury deposition on a glassy carbon electrode (GCE). Cadmium, copper, lead and zinc were monitored simultaneously by anodic stripping voltammetry (ASV) after a sample was flowed through the electrochemical cell for deposition of the metals on mercury film. The detection limit for cadmium, copper, lead and zinc were 4, 7, 1 and 15 ppb, respectively, for deposition time of 20 s. Linear range of calibration graph for all metals was up to 100 ppb. The precision (%RSD, n=11) for 25 ppb of the metals was 2-6%. The system has been applied to determine the trace metals in drinking water and wastewater samples.

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Trace heavy metals are very important in the environment due their serious toxicity although presenting at very low ncentrations and their capable of accumulation in a food chain. e development of new methods for quantifying trace metals is quired and challenged. Most of the sensitive and selective ethods recently available such as ICP-MS, ICP-AES and GF-AS are too expensive and are not practically applied in a eveloping country, i.e. Thailand. Alternative cost-effective ethods based on combination of flow techniques for sample retreatment e.g. preconcentration/separation with some pectrometric detection systems have been proposed.[1-3]

Voltammetry, especially anodic stripping voltammetry is a romising technique for the determination of trace elements.[4] It s relatively low-cost but provides high sensitivity and can be simultaneous determination of multi-elements. However, batch voltammetry consists of a time consuming and a tedious analysis procedure. Flow techniques have been applied to improve the performance of voltammetry.[5,6] For example, lead in blood was determined by hydrodynamic voltammetry in flow system which can be automated and easy to use.[7] Trace copper in water has been determined in a flow system after on-line extraction as its diethyldithiocarbamate into toluene.[8]

In this work, attempt has been made to develop a flow anodic stripping voltammetry for the simultaneous determination of cadmium, copper, lead and zinc. The optimum conditions of the system were investigated. Several advantages were gained such as better sensitivity and peak resolution, lesser sample and reagent consumption, and faster than batch method. Mercury film electrode can be repeatedly used more than 80 times. The proposed method has been applied to determine the trace metals in drinking water and wastewater samples.

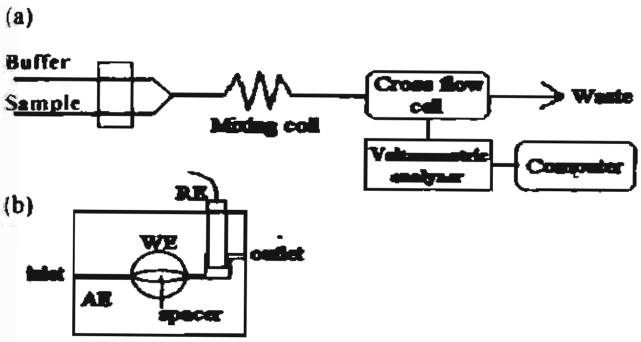
## Experimental

### *Chemicals*

All chemicals were of analytical reagent grade and Milli Q water (millipore) was used throughout for preparing of solutions. Acetate buffer (1 M) was prepared by dissolving 68.04 g of sodium acetate trihydrate (Merck, darmstadt, Germany) in water and glacial acetic acid (Merck) was added until pH of solution was 4.6, then diluting to 500 ml with Milli Q water. The solution was made up to 1000 ml with water. Other concentrations of buffer solutions were prepared by diluting 1 M buffer with Milli Q water. Mercuric nitrate (Merck) was used to prepare a plating solution. Oxygen free nitrogen gas (99.9995 % $N_2$) was used for purging of dissolved oxygen from a solution. A 100 ppm mixed standard stock solution of cadmium, copper, lead and zinc were prepared from a 1000 ppm standard solutions for AAS of each ion (Merck). Other concentrations of mixed standard solutions were prepared by appropriate diluting of a stock solution. Bottled drinking water samples were purchased from locally department stores.

### *Flow manifold*

Two lines manifold was designed as shown in Fig. 1. Sample and acetate buffer solution were pumped with the same flow rate to merge together and flowed further to a mixing coil and a flow through electrochemical cell. Three electrodes cross flow cell (BAS, Indiana, USA) was employed. A voltammograph (BAS CV-50W, BAS) was used for square wave anodic stripping voltammetric analysis. All potentials were measured with respect to a Ag/AgCl reference electrode. A potential of working electrode, mercury thin film coated on a glassy carbon trode was set at –1100 mV for a specified (deposition) time le the sample was flowing through the electrochemical cell. n the flow was stopped and the working electrode was lied by a square wave potential waveform that was swept n –1100 mV to +280 mV, while the current was measured. voltammogram was recorded. The flow was started again to in the electrode and the line, and to prepare for the next iple. For electrochemical cleaning, the potential of the king was set to 0 mV for 20 s.



. 1 Flow diagram of flow voltammetric system: (a) flow nifold and (b) details of flow cell; AE = auxiliary electrode, E = working electrode and RE = reference electrode.

*alysis of samples*

The drinking water samples were degassing by purging with ygen free nitrogen gas before subjecting to analyze by the oposed system. The samples were also analyzed by graphite rnace atomic absorption spectrometry (GF-AAS) as a standard ethod for comparison. The recommended conditions for GF-AS were employed.[9] Wastewater samples were digested efore taking to analyze by the above methods. UV digestion as carried out by adding hydrogen peroxide (30%w/v/) to the mple and irradiating in a home-made UV digestion unit for 6 . The digested solution was put in a 50 ml volumetric flask and iluted to the mark with Milli Q water.

## esults and discussion

*reparation of mercury film electrode*

Mercury film coated on a glassy carbon electrode (GCE) was used as a working electrode (WE). Coating of Hg on a GCE was carried out by applying potential of -800 mV to GCE while flowing a plating solution (500 ppm $Hg^{2+}$ in a 0.1 M $HNO_3$) through the flow cell. The resulted WE was tested for the determination of 100 ppb Cd standard solution. The WE could be repeatedly used for at least 80 analysis cycles, without the deviation of the peak height obtained more than 2% as shown in Fig. 2. The electrochemical cleaning of WE by applying a potential of 0 mV for 20 s after each analysis run was necessary for preventing of cross contamination of the metals.

*Optimization*

*Flow rate.* Flow rate of buffer and sample solutions were equal. Total flow rate of the system was optimized in order to get higher peak currents and good reproducibility. It was found that the higher flow rate provided the higher sensitivity and sample through put, but for flow rate of more than 0.5 ml $min^{-1}$, the deterioration of mercury film was observed and leading to low reproducibility of the results. Total flow rate of 0.5 ml $min^{-1}$ was chosen for further studies.

*Concentration of buffer solution.* Acetate buffer concentrations (0.2-1.0 M) were studied. The effect of buffer concentration on peak current of 70 ppm Cd and Pb was shown in Fig. 3. 0.5 M Acetate buffer was chosen because the higher sensitivity and reproducibility of peak heights were obtained.

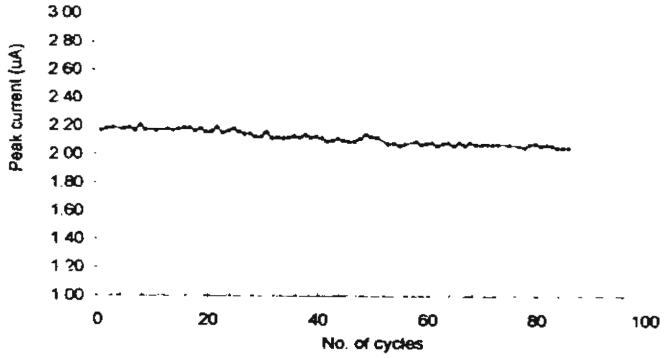


Fig. 2 Peak current of 100 ppb Cd for several analysis runs using the same mercury film.

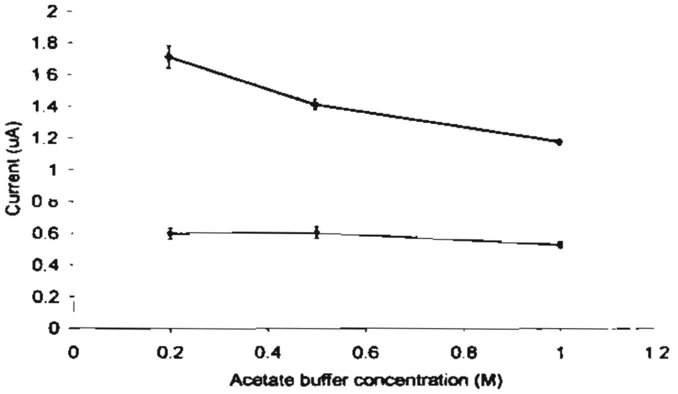


Fig. 3 Effect of buffer concentration on peak current of: (a) Cd and (b) Pb.

*Mixing coil length.* Mixing coils of 0, 50, 100 and 150 cm long have been tried. The length of mixing coil did not much affect the peak height, but did affect the precision of analysis. The mixing coil of 100 cm long was chosen due to the lowest %RSD of peak heights for all metals and rapid analysis were obtained.

The optimum conditions for flow anodic stripping voltammetry were summarized in Table 1.

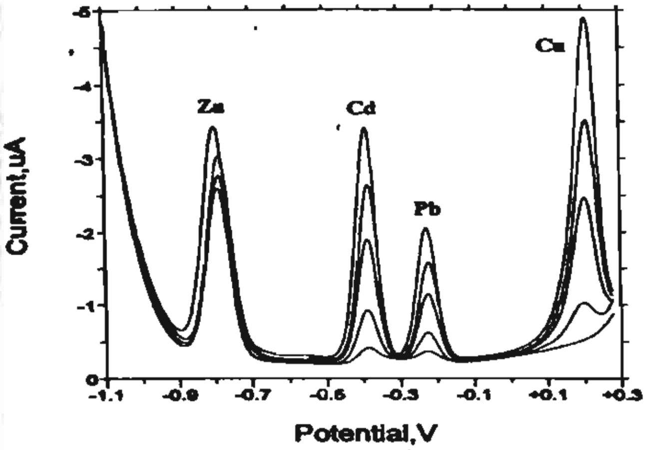
Table 1 Optimum conditions for flow voltammetric system for the determination of Cd, Cu, Pb, and Zn.

| | |
|---|---|
| Mercury plating | 500 ppm Hg(II); -800 mV;10 min |
| Electrolyte | 0.5 M Acetate buffer pH 4.6 |
| Flow rate (total) | 0.5 ml $min^{-1}$ |
| Mixing coil length | 100 cm |
| Electrolysis potential | -1100 mV vs Ag/AgCl |
| Stripping (sweep) potential | -1100 to 280 mV |
| Sweep mode | Square wave |
| Sweep rate | 75 mV $s^{-1}$ |

*Calibration graph and precision*

Using conditions in table 1, a series of mixed standard solutions of cadmium, copper, lead and zinc (5, 20, 50, 70 and

00 ppb) was analyzed. The voltammograms obtained are epicted in Fig. 4. A calibration graph of each metal was onstructed by plotting peak current (μA) as y-axis versus oncentration (ppb) as x-axis. The linear ranges, calibration quations, $R^2$ and detection limits (3σ) are presented in Table 2.



ig. 4 voltammograms obtained from flow-ASV system; 5, 20, 50, 70 and 100 ppb each element.

Table 2 Calibration data for various elements.

| Element | Linear range | Equation | $R^2$ | Detection limit (ppb) |
|---|---|---|---|---|
| Cd | 5-100 | $y=0.032x + 0.05$ | 0.9956 | 4 |
| Cu | 10-100 | $y=0.043x + 0.50$ | 0.9982 | 7 |
| Pb | 5-100 | $y=0.017x + 0.02$ | 0.9986 | 1 |
| Zn | 20-100 | $y=0.007x + 1.20$ | 0.9440 | 15 |

Precision of the method was evaluated by 11 replicate determinations of 25 ppb each element in a mixed metals standard solution. The relative standard deviation of Cd, Cu, Pb and Zn were found to be 3.8, 6.2, 3.6, 3.0, respectively.

*Analysis of samples*

The results of analysis of drinking water samples are shown in Table 3. Concentrations of the metals in bottled drinking water samples were less than detection limits, except Zn in Mont Fleur drinking water. The recovery of all metals is in range of 95-105 % for the standard addition of 25 ppb each element into an aura sample.

Table 3 Analysis results of drinking water samples.

| Sample | Concentration found (ppb) | | | |
|---|---|---|---|---|
| | Cd | Cu | Pb | Zn |
| Cooly fresh | - | - | - | - |
| Aura | - | - | - | - |
| Polaris | - | - | - | - |
| Mont Fleur | - | - | - | 112 |
| Hawiian | - | - | - | - |
| Minere | - | - | - | - |
| Vittel | - | - | - | - |
| Perrier | - | - | - | - |
| S. Pellegrino | - | - | - | - |

- = below detection limits.

Concentrations of Cd and Pb in digested wastewater samples are shown in Table 4. The results obtained agreed with those obtained from GF-AAS method.

Table 4 Concentrations of Cd and Pb in digested wastewater samples.

| Sample | Concentration found (ppb) by method | | |
|---|---|---|---|
| | GF-AAS | Flow-ASV | %different |
| Cadmium | | | |
| S1 | 25 | 26 | 4 |
| S2 | 50 | 54 | 8 |
| S3 | 7 | 4 | -42 |
| Lead | | | |
| S1 | 100 | 92 | -8 |
| S2 | 200 | 196 | -2 |
| S3 | 20 | 28 | 40 |

A flow voltammetric system was developed. Under suitable conditions, the system could be applied for the simultaneous determination of trace cadmium, copper, lead and zinc using anodic stripping voltammetric mode. The sensitivity and selectivity (peak resolution) were improved from the conventional batch voltammetric system because a large area and thin mercury film electrode was employed. The same mercury film could be repeatedly used for at least 80 analysis runs. The proposed procedure consumed less sample and reagent, and was faster than a batch method. The system provided opportunity for automation and incorporation of on-line sample pretreatments.

## Acknowledgements

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# ภาคผนวก ง

UV- digestion for determination of some metals in treated wastewater by anodic stripping voltammetry.

# UV-DIGESTION FOR DETERMINATION OF SOME METALS IN TREATED WASTEWATER BY ANODIC STRIPPING VOLTAMMETRY

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Keywords: UV-digestion, Metals, Wastewater, Anodic Stripping Voltammetry

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## Abstract

A study on sample pretreatment by UV-digestion for determination of some metals (Zn, Cd, Pb and Cu) in wastewater using anodic stripping voltammetry (ASV) was performed. An UV-digester was home-made. A model sample of treated wastewater from a chemistry laboratory (Department of Chemistry, Chiang Mai University) was mixed with $H_2O_2$ and was UV irradiated. Effect of irradiation time was studied. Samples before and after digestion were analysed by using square wave ASV (SWASV) with hanging mercury drop electrode (HMDE) as a working electrode (WE), Ag/AgCl (in 3 M KCl) as a reference electrode (RE) and platinum wire as a counter electrode (CE). The electrolyte solution was acetate buffer (pH 4.6).

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# ภาคผนวก จ

Efficiency in reducing of arsenate to arsenite by sodium thiosulphate.

# ประสิทธิภาพในการรีดิวซ์อาร์ซีเนตเป็นอาร์ซีไนต์โดยใช้โซเดียมไธโอซัลเฟต
# EFFICIENCY IN REDUCING OF ARSENATE TO ARSENITE BY SODIUM THIOSULPHATE

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**บทคัดย่อ** : ได้ศึกษาถึงประสิทธิภาพในการรีดิวซ์อาร์ซีเนต ($As^{5+}$) ไปเป็นอาร์ซีไนต์ ($As^{3+}$) โดยใช้โซเดียมไธโอซัลเฟตเป็นตัวรีดิวซ์ ทำการตรวจวัดเพื่อหาปริมาณอาร์ซีเนตก่อนการรีดิวซ์เทียบกับหลังจากถูกรีดิวซ์แล้วโดยใช้เทคนิคสเปกโทรโฟโตเมตรี ที่ใช้โมลิบเดตเป็นรีเอเจนต์ ตรวจวัดการดูดกลืนแสงของสารประกอบโมลิบโดอาร์ซีเนต ที่ความยาวคลื่น 886 นาโนเมตร และพบว่าสามารถรีดิวซ์อาร์ซีเนตในช่วงความเข้มข้น 10 - 50 พีพีเอ็ม ได้ทั้งหมดโดยใช้ $2.4 \times 10^{-4}$ โมลาร์ โซเดียมไธโอซัลเฟต

**Abstract:** Efficiency in reducing of arsenate ($As^{5+}$) to arsenite ($As^{3+}$) by sodium thiosulphate had been studied. Arsenate contents before and after the reduction were determined by spectrophotometry using molybdate as a coloring agent. The absorbance of molybdoarsenate was measured at 886 nm. It was found that arsenate in concentration range of 10 – 50 ppm can be completely reduced using $2.4 \times 10^{-4}$ M sodium thiosulphate.

**Methodology:** The standard solutions of arsenate (10, 20, 30, 40 and 50 ppm) in 0.3 M sulphuric acid and $2.4 \times 10^{-4}$ M sodium thiosulphate were prepared. After standing the solution for 5 min at the room temperature, 0.01 M hydrochloric acid and 0.001% (w/v) molybdate solution were added. Then the mixed solution was allowed for color development for 4 hours. The absorbance of molybdoarsenate was measured at 886 nm. A calibration graph for arsenate in concentration range of 0.20 – 1.00 ppm was constructed by performing the experiment as above, except without addition of sodium thiosulphate.

**Results, Discussion, and Conclusion:** A calibration graph of arsenate over the range of 0.2 – 1.00 ppm was established (as shown in Figure 1). The detection limit was 0.04 ppm $As^{5+}$. It was found that the solution of 10 - 50 ppm arsenate treated with $2.4 \times 10^{-4}$ M sodium thiosulphate gave the absorbance at 886 nm less than the detection limit of the method. Therefore the procedure was very effective to reduce arsenate in concentration range of 10 – 50 ppm.

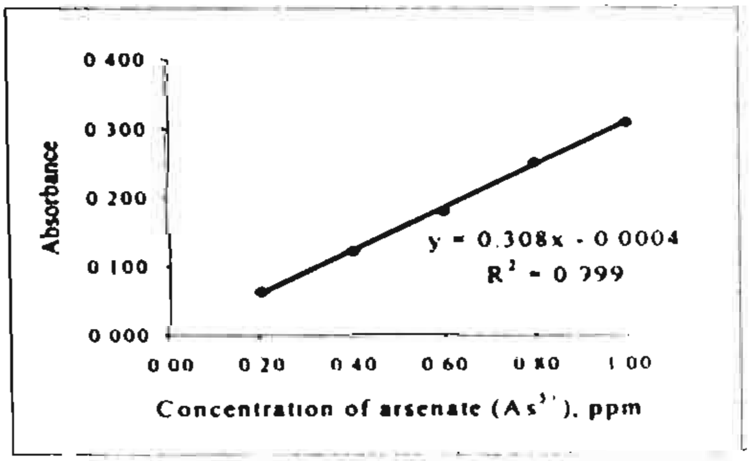

**Figure 1** Calibration graph of arsenate ($As^{5+}$)

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**Keywords:** arsenate, arsenite, spectrophotometry, reduction, thiosulphate

# ภาคผนวก ฉ

Fabrication and performance test of a simple voltammograph for teaching.

# การสร้างและทดสอบประสิทธิภาพเครื่องโวลแทมโมกราฟอย่างง่ายสำหรับการเรียนการสอน

# FABRICATION AND PERFORMANCE TEST OF A SIMPLE VOLTAMMOGRAPH FOR TEACHING

จรูญ จักร์มุณี, เอกชัย แซ่ย่าง, ดุสิตา นุชนิยม และเกตุ กรุดพันธ์*
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**บทคัดย่อ :** ได้ออกแบบและสร้างเครื่องโวลแทมโมกราฟอย่างง่ายขึ้นโดยใช้วัสดุที่หาได้ในประเทศไทย เครื่องมือที่สร้างขึ้นสามารถเปลี่ยนศักย์ในรูปของดีซีแรมพ์ จึงสามารถใช้ในดีซีโพลาโรกราฟี ลิเนียร์สแกนโวลแทมเมตรี ไซคลิกโวลแทมเมตรี และแอมเพอโรเมตรี ได้ทำการทดสอบประสิทธิภาพของเครื่องมือโดยใช้ดัมมีเซลล์ และศึกษาไซคลิกโวลแทมเมตรีของสารละลายเฟอริไซยาไนด์ เครื่องมือที่สร้างขึ้นได้ใช้ในวิชาปฏิบัติการการวิเคราะห์เชิงไฟฟ้าเคมีของนักศึกษา

**Abstract:** A simple voltammograph was designed and fabricated using materials available in Thailand. The instrument can sweep the potential in form of DC ramp, so it can be used for DC polarography, linear scan voltammetry, cyclic voltammetry and amperometry. The performance tests of the instrument by using a dummy cell and studying of cyclic voltammetry of ferricyanide solution were performed. The developed instrument was used in electroanalysis laboratory for students' exercises.

**Methodology:** A three electrode system voltammograph was fabricated using electronic parts locally available (e.g. operational amplifier, resistors, switches, etc.). It consisted of different circuits such as a DC ramp generator, a potentiostat and a current measurement. The instrument was tested using a dummy cell (1000 Ω resister) or solutions of $K_3Fe(CN)_6$ in 1 M $KNO_3$ by scanning a potential of working electrode (WE, Pt disc) from +650 to 0 and back to +650 mV vs Ag/AgCl, against Pt wire auxiliary electrode. The potential of WE ($E_{WE}$) and current passing across the WE ($I_{WE}$) was monitored by a multimeter and recorded on a x-t recorder during the scanning.

**Results, Discussion, and Conclusion:** From the cyclic voltammetry test using a dummy cell, a graph between $E_{WE}$ or $I_{WE}$ versus time was a triangular shape. A scan rate ($mVs^{-1}$) and a gain of the current measuring circuit was evaluated from the graphs. The cyclic voltammograms of $K_3Fe(CN)_6$ are shown in Fig. 1. The peak currents for cathodic and anodic scanning were resulted from the reduction and oxidation of following reaction:

$$Fe^{III}(CN)_6^{3-} + e^- \quad = \quad Fe^{II}(CN)_6^{4-}$$

The peak current increased linearly with the concentration of $K_3Fe(CN)_6$ and the scan rate.

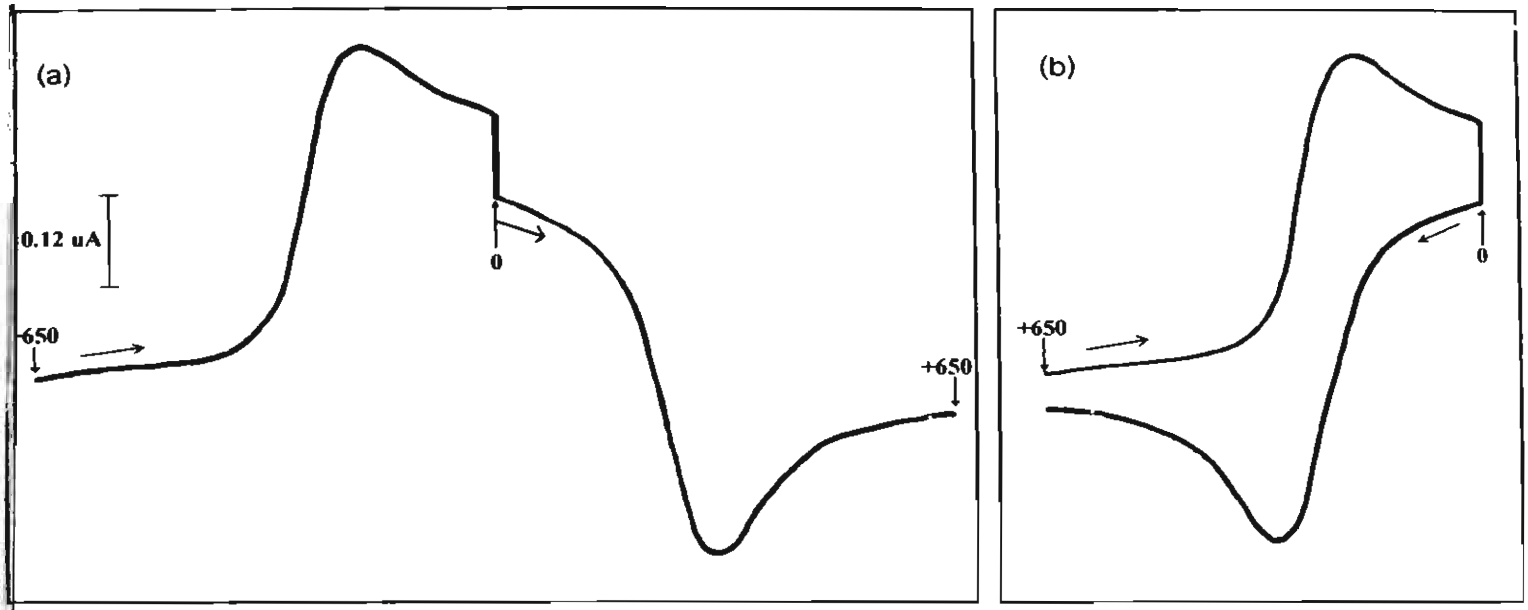

**Figure 1** cyclic voltammogram of potassium ferricyanide obtained from (a) x-t recorder and (b) after further processing; (2 mM $K_3$ Fe $(CN)_6$ in 1 M $KNO_3$, scan rate 10 mV $s^{-1}$).

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**Keywords:** voltammograph, cost-effective instrument, cyclic voltammetry, laboratory exercises