รายงานวิจัยฉบับสมบูรณ์

โครงการการทำไอระเหยเพื่อความจำเพาะเจาะจงในการวิเคราะห์และการออกแบบอุปกรณ์

โดย ดวงใจ นาคะปรีชา

30 มีนาคม 2552

สัญญาเลขที่ **RMU4880038**

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ดวงใจ นาคะปรีชา

ภาควิชาเคมีและศูนย์นวัตกรรมทางเคมี

คณะวิทยาศาสตร์ มหาวิทยาลัยมหิดล

สนับสนุนโดยสำนักงานกองทุนสนับสนุนการวิจัย

และสำนักงานคณะกรรมการการอุดมศึกษา

กิตติกรรมประกาศ

คณะผู้วิจัยใคร่ขอขอบคุณสำนักงานกองทุนสนับสนุนการวิจัย และ สำนักงานคณะกรรมการการอุดมศึกษา ที่ได้เล็งเห็นความสำคัญของการพัฒนาศักยภาพของนักวิจัยรุ่นกลาง โดยให้การสนับสนุนในรูปของทุนวิจัยร่วม เพื่อเน้นให้ผลิตผลงานตีพิมพ์ออกสู่วารสารวิชาการระดับนานาชาติ และขอขอบคุณที่ได้ให้ความไว้วางใจกับนักวิจัยและเล็งเห็นถึงความสำคัญของโครงการวิจัยเรื่องนี้ และได้อนุมัติให้ทุนสนับสนุนการวิจัยดังกล่าว

คณะผู้วิจัยขอขอบคุณศูนย์นวัตกรรมทางเคมี (PERCH-CIC) ที่ได้สนับสนุนทุนการศึกษาแก่นักศึกษาระดับปริญญาโทและปริญญาเอกจำนวน 4 คนในโครงการวิจัยนี้ ตลอดจนค่าวัสดุวิจัยบางส่วนและให้ความเอื้อเฟื้อสนับสนุนครุภัณฑ์ที่ใช้ในโครงการวิจัยนี้ทั้งหมด

สุดท้ายนี้คณะผู้วิจัยใคร่ขอขอบคุณ ภาควิชาเคมี และคณะวิทยาศาสตร์ มหาวิทยาลัยมหิดล ที่ได้ให้การสนับสนุนทั้งทางตรงและทางอ้อม ตลอดจนการอำนวยความสะดวกต่าง ๆ จนงานวิจัยนี้สำเร็จลุล่วงด้วยดี

บทคัดย่อ

ในงานนี้ได้มีการพัฒนาเทคนิคใหม่เพื่อการแยกเรียกว่า การแยกแบบไร้เยื่อเลือกผ่าน ซึ่งเหมาะอย่างยิ่งสำหรับการนำมาประยุกต์กับเทคนิควิเคราะห์แบบไหล ซึ่งการแยกแบบไร้เยื่อเลือกผ่านนั้น ได้พัฒนาขึ้นสำหรับทั้งการแพร่ของแก๊ส และสำหรับการแปลงสารให้เป็นไอระเหยก่อนแล้วจึงทำการแพร่เพื่อแยก ซึ่งในงานนี้นั้นได้ออกแบบการทดลอง และพัฒนาให้เห็นเป็นรูปธรรมถึงการนำเอาหลักการแยกแบบใหม่นี้มาใช้กับการวิเคราะห์แบบไหล ซึ่งเหมาะจะเป็นเทคนิคการวัดที่รวดเร็วและแม่นยำ อีกทั้งได้ทำการพิสูจน์ให้เห็นชัดเจนว่าการถ่ายเทมวลของแก๊สในระบบไร้เยื่อเลือกผ่านนั้นสูงกว่าเมื่อใช้เยื่อเลือกผ่าน ซึ่งการเลือกปฏิกิริยาเคมีที่จำเพาะเจาะจงในการทำไอระเหยนั้นจะเพิ่มความจำเพาะเจาะจงของสารที่จะทำการวิเคราะห์ได้อย่างดี

ได้พัฒนาระบบขึ้นมาทั้งสิ้น 3 ระบบด้วยกันที่มีการนำการแยกแบบไร้เยื่อเลือกผ่าน มาใช้ ซึ่งทุกระบบก็ได้พิสูจน์ให้เห็นประสิทธิภาพของการแยกชนิดนี้ เช่น การวิเคราะห์เอทานอลในเครื่องดื่มแอลกอฮอล์ การวิเคราะห์สารคาร์บอเนตในของเหลวและของแข็ง และ การวิเคราะห์การปนเปื้อนสารหนู นอกจากนี้ยังได้ทำการศึกษาการแยกชนิดเดิมที่มีการใช้เยื่อเลือกผ่าน เรียกว่า เพอแวพอเรชั่นด้วย เพื่อให้มีประสบการณ์และเพื่อจะได้ทำการเปรียบเทียบกับการแยกชนิดไร้เยื่อเลือกผ่านที่ได้พัฒนาขึ้น ซึ่งพบว่าในกรณีการวิเคราะห์ไอโอไดด์โดยแปลงเป็นไอโอดีนแก๊ส ก่อนเพื่อทำการแยกแก๊สนั้นไม่เหมาะสมกับเทคนิคใหม่ที่พัฒนาขึ้น ซึ่งพบว่าหลักการเพอแวพอเรชั่นนั้นจะเหมาะสมกว่าในกรณีการวัดไอโอไดด์ในเม็ดวิตามินรวม

Abstract

Project code: RMU4880038

Project title: Formation of volatile compounds for selectivity in analysis with design of gas collection unit

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Project period: 29 July 2005 to28 July 2008

This work was carried out to develop a new separation technique suitable for flow analysis called 'membraneless technique'. The membraneless technique was developed for gas diffusion or for evaporation of gas in order to separate analyte from the matrix. This work has demonstrated that the principle of membraneless (for gas diffusion and for vaporization) is practical especially when coupled with flow analysis for increasing the throughput and precision. It has been proved that the mass transfer efficiency is greater without use of membrane. Nontheless, specificity of the separation is still achievable from selective chemical reaction for vaporization process.

In this work, three systems have been set up and demonstrated for the efficacy of the membraneless principle. The systems include analyses of ethanol in alcoholic drink, carbonate in liquid and solid sample and arsenic contamination. Beside, investigation of a membrane based technique called 'pervaporation' was carried out for gaining experience and for comparison with our current membraneless system. It was found for iodine analysis that pervaporation is a better of technique than the membraneless technique. A new method for determination of iodide using pervaporation was developed for analysis of multivitamin tablets.

Future work, could be further investigation for utilize the principle of membraneless vaporization for making a portable kit for wine analysis.

Keywords: membraneless, vaporization, gas diffusion, pervaporization

Introduction

1. Background and principles

1.1 Background

Most analytical procedures involve at least a separation step in sample preparations. Separations can be carried out by different means such as liquid-liquid extraction, liquid-solid extraction and other types of sample clean up. Generally the purpose of separation is usually to increase the selectivity of determination by separating analyte from the surrounding substance which contains some interference for chemical analysis. Our group has been working with iodine analysis for a period [1-9]. We explicitly think that there are still lots to play with halogens for the purpose of separation. This also applies to other analytes, either by straight detection of the existing volatile analyte or by conversion of species prior detection.

1.2 Principle for improving the selectivity

Elementary halogens themselves exist naturally in gaseous form. These elements in group VII of the periodic table all have varieties of oxidation states. Thus, there are many ways to convert the elements into several forms simply by using the right reagent either as oxidising or reducing agents. Again through our experience with iodine analysis, we think it will be very interesting to exploit these properties of halogens for improving the selectivity in quantitative analyses.

An example to use some halogen chemistries for chemical analysis is shown in reaction 1 and 2. We can employ both reactions 1 and 2 to generate elementary iodine (I_2). Reaction 1 is used when our analyte exists in the sample as iodide ion (I^-). To generate I_2 we use an appropriate oxidant such as dichromate ion. Similarly, reaction 2 is the method for producing the gaseous iodine starting from iodate ion (IO_3^-). This time a reducing agent such as iodide ion or other suitable reductants can be used.

Oxidation: $2\mathbf{I}^-_{(aq)} + Cr_2O_7^{2-}{}_{(aq)} + 14H^+_{(aq)} \longrightarrow \mathbf{I_2}_{(aq)/(g)} + 2Cr^{3+}_{(aq)} + 7H_2O$ (1)

Reduction: $\mathbf{IO_3}^-_{(aq)} + 5I^-_{(aq)} + 6H^+_{(aq)} \longrightarrow 3\mathbf{I_2}_{(aq)/(g)} + 3H_2O$ (2)

Reaction 1 and 2 both give elementary iodine as the product, although starting from different iodine species. When mixing all of the reactants, some of the iodine product volatiles from the solution mixture. If we do this in a close system, it is possible to selectively detect only the vapor of molecular iodine above the liquid mixture. Nevertheless this is technically a time dependent procedure, and can be perform awkwardly if the experiments are to be carried out in a manual process. We therefore think that this idea (turning the analyte into gas followed by detection) would work out best by operating in an automatic time-based system.

In this work, we hence propose a project that employs selective gas monitoring with continuous flow-based techniques. The possible techniques are flow injection (FI) and its later generations, e.g., sequential injection (SI) and all injection analysis (AIA). Besides a newly designed apparatus for selective detection will be focussed.

2. Automation techniques based on membrane permeation

Automation usually relies on continuous flow of liquids in small tubing. There have been some reports that employ porous hydrophobic membranes for the separation of volatiles compounds from liquid stream. These techniques are known as "gas-diffusion" and "pervaporation".

(a) Gas diffusion

Gas diffusion (GD) technique is used in FI to transfer a gaseous compound from one stream to the other stream. The two streams are separated by a suitable gas permeable membrane. These two streams are often known as "donor" and "acceptor" (Fig. 1a). The gaseous analyte is partially transferred from the donor (usually sample) into a new matrix of the acceptor stream, which contains no interference. Thus the analyte is now clean and suitable for further detection [10].

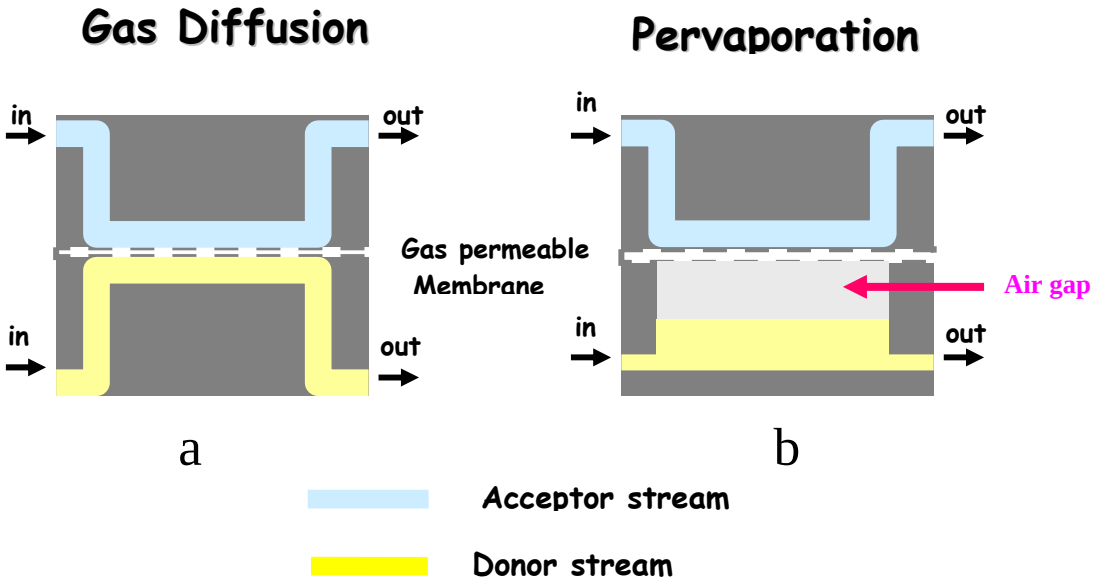

Fig. 1 Schematic diagram showing (a) Gas-diffusion unit and (b) Pervaporation unit.

(b) Pervaporation

Pervaporation (PV), is another membrane-based separation technique which has long been employed in industry. PV has recently been proposed for analytical purposes to overcome problems arising from the use of biosensors in on-line fermentation monitoring [11]. Analytical pervaporation can be defined as the integration of evaporation, gas diffusion and permeation of analyte through a membrane in a single module. Fig. 1b presents the schematic drawing of a PV unit. The volatile substances present in a donor phase evaporate and diffuse through a hydrophobic membrane and the vapour dissolves back to an acceptor solution flowing on the other side of the membrane. The vapour pressure difference across the membrane is the driving force for the separation. An important characteristic of PV is the presence of a constant-volume air gap between the sample in the donor solution and the membrane, which hinders any contact between them, thus avoiding clogging and/or deterioration of the membrane.

PV seems to be a viable alternative to gas diffusion. Comparing to GD, PV has a disadvantage. The air gap decreases the mass-transfer efficiency through the membrane, thereby decreasing the sensitivity of the method. However, PV offers considerable advantages when used with liquid suspension samples and particularly when solid samples are directly treated in the donor chamber. This can not be done in a GD unit. Since only one side of the membrane contact with the acceptor solution, in which the composition is strictly controlled, and it's pores are protected from clogging by suspended particles or components of high molecular

weight that are occasionally present in the sample. With this increased lifetime of the membrane, the PV technique is useful in routine analysis and suitable for automation.

3. The proposed membraneless technique for collection of volatile compounds

We think the idea of using a membrane with gas permeation for improving the selectivity in both the GD and the PV is useful and handy. However these might not be so cost-effective in some cases where membrane needs changing quite often. Also using a membrane can somehow reduce the sensitivity. There might be an alternative way of, still exploiting the idea, but without using any membrane.

It is possible to make two parallel grooves inside a closed module for which the diffusion of gas takes place, but this time between both open channels. This can of course be applied in any automation techniques (FIA, SIA etc.). Fig. 2 is an example of a possible set up of the module. This system requires no membrane at all.

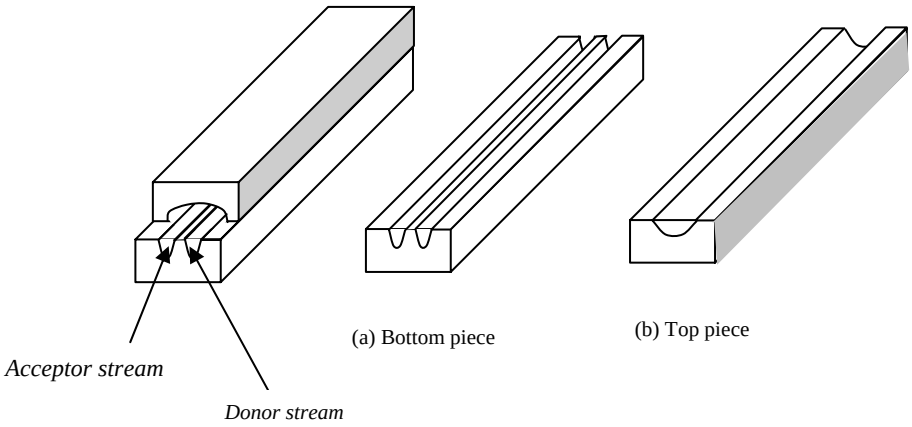

Fig. 2 New design of a membraneless unit for volatile collection. The unit consists of two pieces of Perspex block (a and b).

This idea of such a construction (Fig. 2) is new and no one has done it before. We think that the sensitivity should be better than the concepts of GD and PV since the mass transfer should be greater. This configuration of the unit displaying in Fig. 2 or other configurations based on the same principle would fit in perfectly well with most automation techniques.

4. Importance of this work and new knowledge

This work is based on formation of volatile compounds, from the analytes and on the transfer of part of the volatile molecules into an acceptor reagent for further detection. We planned to investigate some feasible reactions of particular analytes for the volatile formation. Also we planned to investigate different apparatus (GD, PV and our newly designed 'membraneless collection unit') viable for the gas transfer, from the donor solution to the acceptor solution. These will be studied and optimized in continuous-flow fashion for convenience.

We expect that our new unit design in Fig. 2 for transferring our volatile compounds would give a better sensitivity than the previous techniques such as the GD and the PV. Some chemical analysis methods will be developed for key compounds such as iodine (human micronutrient, often is an ingredient of pharmaceutical products) and arsenic compounds (toxic to the environment).

5. Aims

5.1 To optimize the design of our 'membraneless collection unit' and test the effeciency (in the term of sensitivity compared to the GD and PV).

5.2 To develop new quantitative methods for the formation of some volatile compounds with new detection system. The methods will be applied to GD and PV techniques for iodine and arsenic determinations.

5.3 To finally apply the method of volatile formation, with the developed detection, to our new apparatus (the 'membraneless collection unit').

6. Literature review

6.1 Application of membrane-based techniques for quantitative analysis

Motomizu and Yoden reported a tubular microporous PTFE membrane that was applied to iodine and other halogens [12]. The permeated halogens react with *N*, *N*-diethyl-*p*-phenylenediamine to produce coloured substances. By coupling this chromogenic reaction with the permeation of halogens, the sensitive and selective determination of halogens and halide ions can be achieved.

In 1997, Hakedal and Egeberg [13] proposed a GD-FI system for determination of iodide in saline water. The procedure was based on the oxidation of the iodide to iodine (I_2), following by permeation through a PTFE membrane into a stream of an iodide carrier. Absorbance of tri-iodide (I_3^-) was measured spectrophotometrically at 350 nm. The detection limit was 0.2 mg I/L when 300 μL and a flow cell at 4-cm path length were used.

There are other applications of membrane-based techniques for some other analytes. However we can develop some new methods for those membrane-based techniques especially for iodine. And this time we will also extend our work to arsenic compounds, which are the key toxic substances in some contaminated area of Thailand.

For arsenic compounds, there have been few works reported concerning PV techniques. Detection of arsine on the acceptor's side, after hydride generation, are either based on decrease of permanganate visible absorption [14] or on the molybdenum blue method [15]. None of it has been reported on use of a collection unit, which has no membrane like our work.

6.2 Application of the membraneless technique

None has ever been reported until this work.

Methodology

7. Research plan and methodology

7.1 Design and optimization of the new 'membraneless collection unit'

First we designed and constructed two prototypes of the collection unit, which do not employ membrane. One is flat-rectangular shape with two parallel grooves for gas diffusion. The other design is a round configuration. The system was tested with system of ethanol and carbon dioxide vaporizations. Also arsenic analysis was planned to be investigated using membraneless vaporization via conversion to arsine gas.

7.2 Method developments for volatile formation of analytes and for sensitive detection

This part of work will firstly employ the two established membrane permeation techniques that are GD and PV. Although these two techniques have already been reported but we will apply these two techniques with our newly development methods of analysis.

7.3 Comparison with membrane-based technique

Some of the study was planned to compare with conventional membrane-based method such as gas diffusion (GD) or pervaporation (PV).

Results and Discussions

8. Work on 'Membraneless' and 'Membrane-based'

The work can be separated into 4 parts including

(i) First design of membraneless unit and the demonstration of the technique in ethanol analysis was carried out.

(ii) Second design of membraneless unit was made to improve some minor drawback of the first design. This second design was made and used in method development for carbonate analysis. Applications was successful both for liquid and solid samples.

(iii) The third part is use of the second design for developing a new method for determination of arsenic.

(iv) This final part was a method development based on use of membrane-based technique called 'pervaporation' or PV. We first tried to apply the second design of the membraneless unit for iodine analysis but it did not seem to be successful. It is therefore, in some cases, use of a membrane is desirable. In this part we developed a new method for determination of iodine in multivitamin tablets.

The followings are description of ***results and discussions*** of ***parts 1 to 4***.

8.1 Part 1: First design of membraneless unit and its application in ethanol analysis.

8.1.1 Design of the membraneless unit

The designed membraneless gas diffusion unit is illustrated in Fig. 3. The unit contains two parallel channels inside a closed module for which the diffusion of gas takes place between both open channels. These grooves are used as donor and acceptor channels. The unit was designed so that both grooves are separated by the 2 mm-thick barrier (depicted in Fig. 3 a and Fig. 3 b). The height of this barrier is made slightly lesser than the depths of the channels (Fig. 3b). Thus any volatile or semi-volatile compounds can diffuse across this barrier, from the donor side to the acceptor side. With this configuration, separation and detection of the volatile analyte can be done selectively without use of any porous membrane.

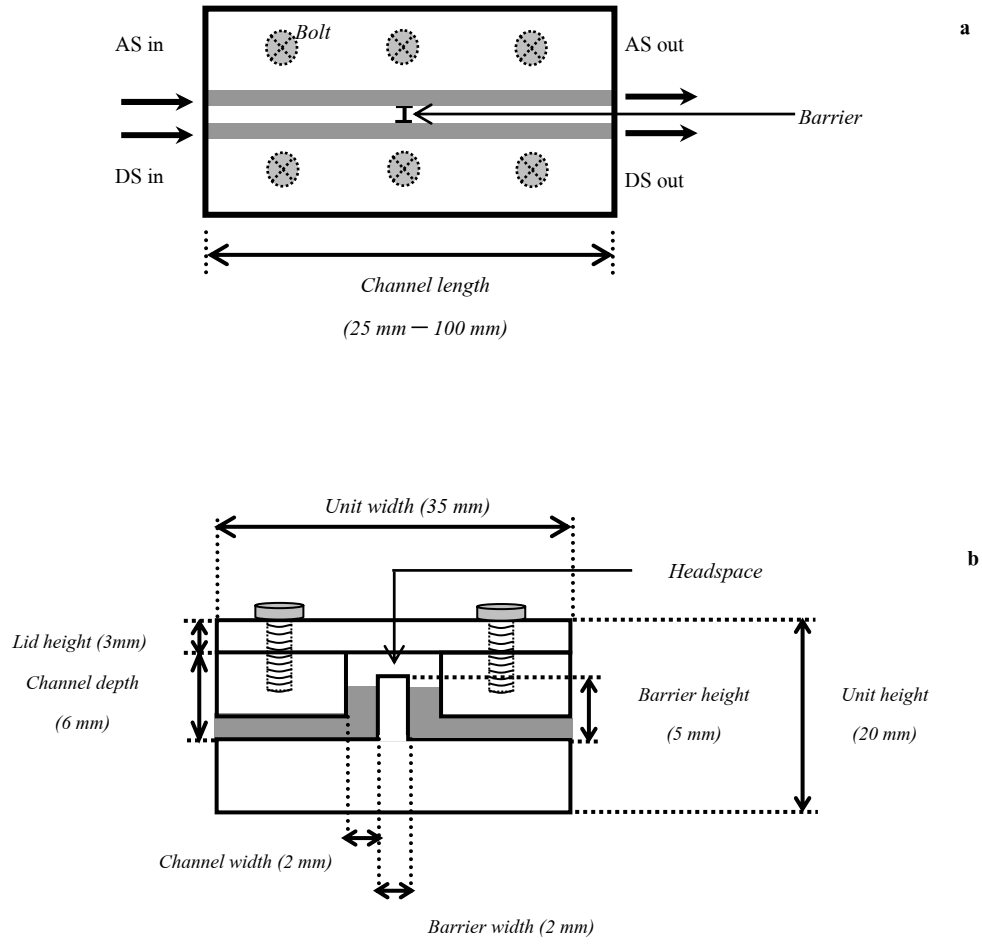

Fig. 3 Schematic diagram of the MGD unit (a) top view; (b) side view.

The depth of the channels must be carefully designed. When the channel depth was shallow (3 mm), creeping of solutions across the barrier was observed. This flooding problem was solved by using the unit with deeper channels (6 mm). As we did this, we also increased the volume of the headspace and this lowered the sensitivity. Nevertheless, we noticed that the sensitivity (for 50-mm channel length) was lowered only by 11 %, when the 6-mm channel depth was used, compared with the 3-mm depth. Thus, the unit with 6-mm depth was selected for further experiments.

8.1.2 *The MGD-FI system*

The MGD-FI system for determination of ethanol is depicted in Fig. 4. The system was automatically controlled by LabView 7.1^{TM}. The peristaltic pump (Cavro, USA) was used with Tygon^{TM} pump tubes (0.79 mm i.d.). A six-port injection valve (SNK, Japan), with a 300-µl injection loop, was employed for injecting standard and sample solutions. A Soma S-3250 spectrophotometer (Japan), equipped with a 10-mm flow-through cell and a FIA monitor/data processing apparatus (F.I.A Instruments, Japan), were respectively utilized for the detection and recording of signals. The manifold in Fig. 4 was constructed by using 0.5 mm i.d. PTFE tubing.

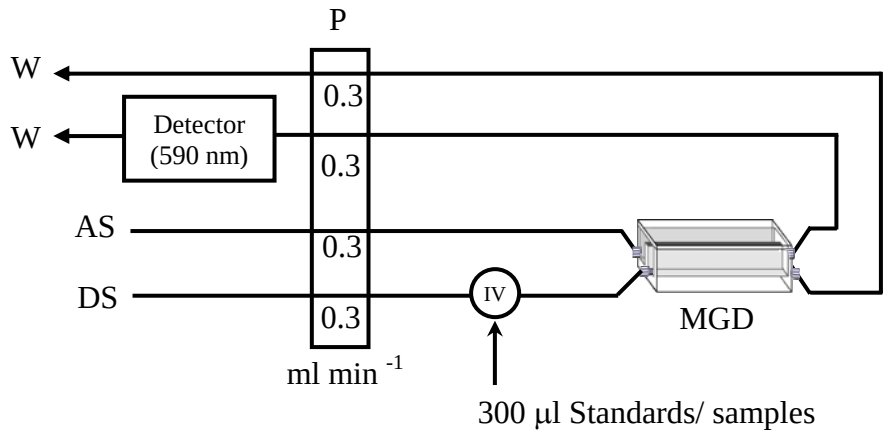

Fig. 4 The FI system for spectrophotometric determination of ethanol. DS: Donor stream (water), AS: Acceptor stream (0.03 mol l^{-1} $K_2Cr_2O_7$ in 1.5 mol l^{-1} H_2SO_4), MGD: Membraneless gas diffusion unit (50 mm-channel length is optimum), IV: Injection valve, P: Peristaltic pump and W: Waste.

8.1.3 Flow rate

Flow rates of the donor and the acceptor stream are one of the most important parameters. Flow rates at the '*inlet*' and the '*outlet*' of donor and acceptor streams must be set equally, to avoid flooding of the MGD channels. This can be done by using the same set of pump tubes for propelling the solutions into and out from the MGD unit (Fig. 4). Operation at high flow rate could increase the throughput. However, this resulted in the decrease in the sensitivity

of the ethanol detection. For this work, the flow rate of 0.3 ml min^{-1} was chosen for all the FI streams.

8.1.4 Influence of temperature

The temperature of donor and acceptor streams can affect considerably both the evaporation of ethanol and its diffusion in the MGD unit. Higher temperature increases the vapor pressure of the analyte in the headspace area inside the unit and accelerates the diffusion of the gas.

In this work, the influence of temperature was investigated by placing the MGD unit inside a hot-dried air box (Model GAS DIF, TCI, Japan). The temperature was varied from room temperature (25 °C) to 50 °C. As expected, the sensitivity was enhanced by increasing the temperature. The average peak height at 50 °C was about 50 % greater than the average height at 25 °C. However, the sensitivity is already sufficient at 25 °C. Therefore, we decided to carry out the analysis at the room temperature, which is the most convenient.

8.1.5 Relative mass transfer compared to membrane-based gas diffusion

Although employment of membrane is very useful and suitable for the designs of GD and PV units, the sensitivity would have been reduced with membrane permeation. In dynamic system, like flow injection, membrane lessen the mass transfer of the gaseous species.

Comparison of the mass transfer efficiency, between the GD-FI and the MGD-FI, is shown in Fig. 5. Although the effective area of donor stream in MGD is 4 times smaller than the GD unit, the mass transfer efficiency of MGD is always greater. This result (Fig. 5) clearly demonstrated that the MGD design is more effective and give a better sensitivity than the GD design. The result also supports that for a dynamic diffusion system like this, membrane can reduce the mass transfer of gas.

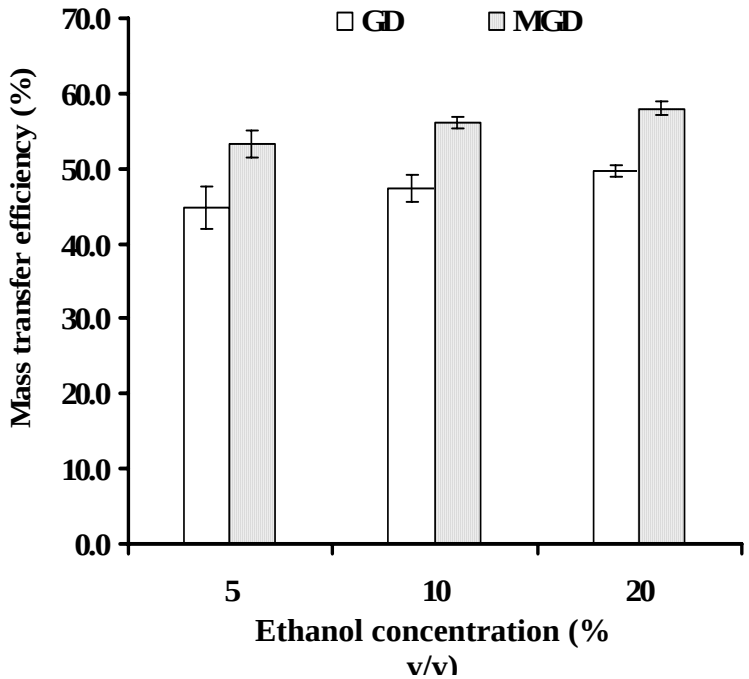

Fig. 5 Mass transfer efficiencies of MGD and GD.

8.1.6 Effect of interference

Effect of foreign species was investigated. The examined species were inorganic mono- and divalent cations and anion, which could be found in wine: Li^+ (500 mg l^{-1}), Na^+ (500 mg l^{-1}), NH_4^+ (250 mg l^{-1}), Mg^{2+}(400 mg l^{-1}), Ca^{2+}(400 mg l^{-1}) and SO_3^{2-} (0.01 M). Ammonia (0.5 M) was also studied because it can be produced during brewing fermentation. Results showed that signal alteration for all species was less than 3 %. This suggests that the developed method is free from interferents in alcoholic drinks.

8.1.7 Applications to liquor sample

The developed system was applied in determination of ethanol. Results of eight alcoholic drinks are shown in Table 1. Statistical analysis (paired-*t* test) showed that the data from MGD-FI are not significantly different to the data from the GD-FI (t_{stat} = 1.43, $t_{critical}$ = 1.89 at 95 % confidence). The measured values also agree well with the labeled values. The recovery test for the same set of samples

shows that recovery ranged from 92.5 % to 109 %. These results therefore approve the validity of the MGD for quantitative analysis of ethanol in beverages.

Table 1 Ethanol contents in beverages determined by the MGD-FI and GD-FI method compared with the labeled values.

Samples	%(v/v) of ethanol, n = 3		
	Labeled	MGD-FI	GD-FI
Beer	5	4.12 ± 0.04	3.77 ± 0.08
Japanese sake 1	10	10.4 ± 0.16	11.1 ± 0.04
Japanese sake 2	14	15.6 ± 0.20	15.9 ± 0.11
Red wine	14	15.7 ± 0.09	16.0 ± 0.14
White wine	14	14.4 ± 0.07	15.9 ± 0.15
Thai whisky 1	35	35.0 ± 0.34	35.5 ± 0.28
Thai whisky 2	35	32.6 ± 0.46	36.5 ± 0.43
Thai whisky 3	40	42.2 ± 0.75	41.2 ± 0.59

8.2 Part II: Second design of membraneless unit and its method development for direct determination of carbonate in liquid and solid

In this second part, an attempt to improve the performance and convenience of use of the unit in part I was investigated. The membraneless gas diffusion unit in part I has a drawback of being a close system. In order to open the unit in the case of flooding of liquid, we had to undo the screws and take the top and bottom piece apart. This was slow and not convenient. Therefore a second unit of the same concept was designed as shown in Fig. 6. A new method for determination of carbonate was successfully achieved from this unit. This has allowed a convenient method for determination of both liquid and solid sample. Direct analysis can be simply done. The method is new. The second unit is easy to use and the problem of flooding of reagents was diminished.

8.2.1 Unit design

Fig. 6 shows schematic diagram of the membranless vaporization (MBL-VP) unit. The unit was constructed using four main parts depicted in Fig. 6a, including (i) acrylic donor holder, (ii) glass donor vial, (iii) silicone gasket (38 mm i.d., 54 mm o.d., 2.0 mm thickness) and (iv) lid made of acrylic. All parts were held together tightly by a stainless steel lock (Fig. 6b). This lock is a quick-type of lock for fast locking and unlocking.

The donor holder was made of one whole piece of acrylic, which has been drilled to have a cylindrical cavity (25 mm diameter and 40 mm height as depicted in Fig. 6a). On top of this donor holder, a circular groove was made (dotted circle lines in Fig. 6a). These two dotted circles represent acceptor channel of the unit. The acceptor channel was made functional in circular shape (Fig. 6c) and half-circular shape (Fig. 6d). For the half-circular shape, only one half of the circle was used as the flow part. At the bottom of acceptor channel, two holes were drilled for inlet and outlet. The lid was made of acrylic that had a hole drilled at the center. This hole was fitted together with an applicator for insertion of a 5-mL syringe. This syringe was for injection of acid reagent.

8.2.2 The flow system

Fig. 7 is a schematic diagram of the flow system with the membraneless vaporization (MBL-VP) unit. This flow system has been used for all experiments concerning development of the MBL-VP method for calcium carbonate. An Ismatec peristaltic pump (model IS7610, Switzerland), with tygon pump tubes (0.89 mm i.d.), was used. An Agilent UV-Vis spectrophotometer (Model 8453, Germany), fitted with a 10 mm flow-through cell with internal volume of 80 µL (Hellma, Germany), was employed for monitoring the absorbance of pH-indicator at 440 nm. PTFE tubes with 0.5 mm i.d. (Cole Parmer, USA) were used throughout. A 5-mL plastic syringe (Nipro, Thailand) was used for acid injection. A magnetic stirrer (Model IKA colorsquid, Germany) was employed with a stirring bar (5 mm diameter and 20 mm length) placed inside glass donor vial (Fig. 6a) for providing a better and faster homogenization between acid and samples.

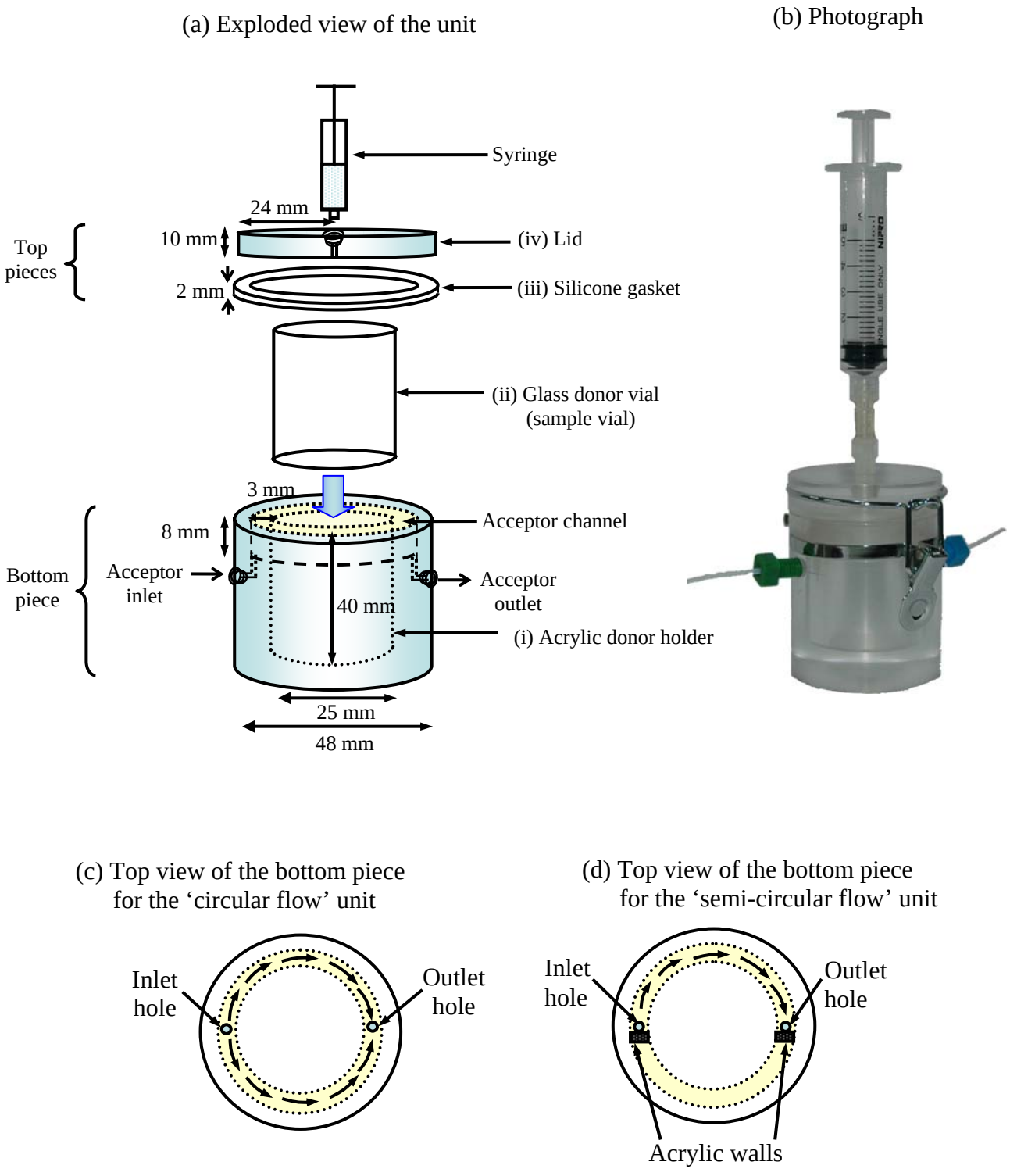

Fig. 6. Schematic diagram and photograph of the membraneless vaporization unit for solid analysis.

Note: Small arrows in the top views (c and d) represent the flow paths.

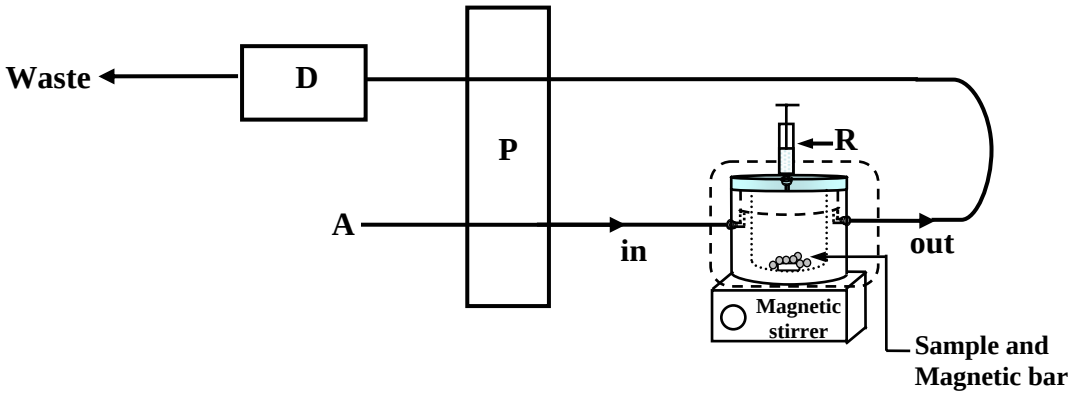

Fig. 7. The flow system with the MBL-VP unit (in the dotted frame) for determination of calcium carbonate. A: acceptor stream. R: acid reagent filled in 5-mL of syringe. P: peristaltic pump. D: spectrophotometer fixed at 440 nm.

8.2.3 Detection and standard calibrator

The detection principle for quantitative analysis of calcium carbonate was based upon reaction. HCl (injected into the MBL-VP unit) solubilized $CaCO_{3(s)}$

$$CaCO_{3(s)} + 2HCl_{(aq)} \longrightarrow CaCl_{2(aq)} + H_2O_{(l)} + CO_{2(g)}$$

in the donor vial and this produced $CO_{2(g)}$. The color of indicator in the acceptor changed accordingly to the pH change, which corresponded to the amount of $CO_{2(g)}$. Use of indicator allowed for simple detection by colorimetry.

Employment of liquid standard solutions was more convenient and rapid than use of solid calcium carbonate. Accurate handling of solid standard for calibration was slightly awkward, because very small amount of ground calcium carbonate must be weighed for each concentration point (2 to 30.5 mg). Thus, for this work, liquid standard solutions were used in the optimization.

Nonetheless, one may think that solid and liquid forms of standard may contribute to different sensitivities in MBL-VP. In order to inspect this, series of standard in solid and liquid forms were tested (0.02 to 0.32 mmol CO_3^{2-}). Calibration equations obtained from $NaHCO_{3(aq)}$ and $CaCO_{3(s)}$ were A_{440nm} = (1.1355 ± 0.0227)mmol CO_3^{2-} - (0.0038 ± 0.0031) and A_{440nm} = (1.1260 ± 0.0287)mmol CO_3^{2-} - (0.0067 ± 0.00395), respectively. These results show that the slopes were almost indistinguishable and intercepts were similar. This indicates that standard in liquid form can be applied, even as calibrator for solid. We therefore employed liquid standards only in the method development for convenience and rapidity. However we used standard powder of calcium carbonate in sample analysis.

8.2.4.Optimization

Optimization has been made accordingly to the followings parameters. Detials of the results can be found in the attached publication.

-Length of acceptor channel

-Operational mode and signal profiles

-Stopped-time

- Flow rate of acceptor stream

8.2.5 Influence of volume and mole of the acid reagent

Effect of volume of acid reagent was investigated (Table 2). Results indicated that the sensitivity increased as the volume of acid decreased. The smaller in depth of the dispensed acid (inside the glass donor vial in Fig. 6a) the better was the sensitivity.

Table 2 Effect of volume of acid reagent on precision and sensitivity studied using standard concentrations from 0.02 to 0.40 mmol CO_3^{2-}. Experiments were carried out at flow rate of 1.6 ml min^{-1} using 0.105 mmol L^{-1} of cresol red as acceptor. HCl was fixed at 5 mmol in the injection of acid.

Volume of HCl / mL	Calibration curve			%RSD for 0.16 mmol CO_3^{2-} (n = 10)
	Slope	Intercept	r^2	
1	1.6944 ± 0.0339	0.0037 ± 0.0071	0.998	2.46
2	1.6353 ± 0.0577	0.0208 ± 0.0121	0.993	2.59
5	1.1447 ± 0.0443	0.0086 ± 0.0063	0.996	10.8

Decreasing in volume of acid reagent (decreasing in depth) had assisted releasing of $CO_{2(g)}$ from the sample vial for reaction with cresol red in the acceptor channel. Moreover, as the volume of acid was increased to 5 mL, reproducibility became poorer, up to about 11 %RSD. Volumes of acid dispensed to the donor vials at 1, 2 and 5 mL resulted in liquid depths at 50, 90 and 160 mm, respectively. Apparently, at 160 mm depth, there were still some submerging bubbles sticking on wall of the vial as well as on the magnetic bar. Occurrence of these bubbles containing $CO_{2(g)}$, caused irreproducible signals (the poorest precision value in Table 2 was from 5 mL acid). The mass transfer efficiency of $CO_{2(g)}$ was better at shallow level of the donor

mixture. Therefore, in this work, 1 mL of acid reagent was chosen because of its best precision. Also the slope given by 1 mL of acid reagent (50 mm depth) was the highest.

The required number of moles of HCl was studied using an amount of ground calcium supplement corresponding to 0.2 mmol $CaCO_{3(s)}$. HCl in acid reagent was varied from 0.01 to 7 mmol. The amount of acid above 0.6 mmol HCl was adequate. However, to avoid other excess requirement of acid such as neutralization, 3 mmol of HCl was chosen as the optimum. Greater amounts of HCl than 3 mmol were not suitable, due to interference from vaporization of the acid itself causing fluctuation of signal.

8.2.6 Analytical performance

Under the optimum condition summarized in Table 3. A linear calibration plot was obtained from 0.02 to 0.4 mmol CO_3^{2-} [$A_{440\ nm}$ = (1.6944 ± 0.0339)mmol CO_3^{2-} – (0.0037 ± 0.0071), r^2 = 0.998]. The detection limits (3S/N) was down to 0.005 mmol of CO_3^{2-}. The method gave good precision with RSD at 2.9% (from ten replicates of 0.16 mmol of CO_3^{2-}). Reasonable throughput at 20 samples h^{-1} was obtained.

Table 3 Optimal condition of the MBL-VP FI system for determination of $CaCO_3$.

Parameter	Studied condition	Chosen condition
Length of acceptor channel / mm	60 and 120	60
Concentration of cresol red / mmol L^{-1}	0.026 - 0.105	0.105
Stopped-time / min	0 - 3	1
Flow rate / mL min^{-1}	0.8 - 2.4	1.6
HCl volume / mL	1 - 5	1
HCl concentration / mmol	0.1 - 7	3

8.2.7. Application and validation

The proposed method was applied to four samples of calcium supplement products. The results were compared with a standard titration method in Table 4. According to paired t-test the results of our method are not significantly different to the results of the titration ($t_{stat} = 0.62$ and $t_{critical} = 3.18$; P = 0.05). The results obtained from the MBL-VP method and the titration seem to agree with the nominal values. Recovery was studied by adding exact amounts of standard powder of $CaCO_3$ into sample vials that contained these calcium supplements. Recovery was observed to range from 93% to 118%, revealing absence of interference effect.

Table 4 Determination of calcium carbonate in calcium supplement tablets by using the MBL-VP method, flame atomic absorption and titration.

Samples	$CaCO_3$ content ($mgCaCO_3$ / tablet), n = 5		
	Nominal	MBL-VP	Titration
Sample A	1500	1375 ± 62	1479 ± 4
Sample B	625	534 ± 8	517 ± 4
Sample C	1500	1469 ± 35	1387 ± 8
Sample D	1000	1076 ± 33	945 ± 4

8.2.8. Conclusions for the second membraneless unit

This work verified effective use of the MBL-VP unit coupled to flow-based technique for direct analysis of solid such as food supplements. A convenient and precise method for quantitative analysis of calcium carbonate was successfully developed using the MBL-VP technique. Membraneless approach should be also useful for other types of samples including liquid and slurry. Application is more versatile than the earlier model for liquid sample. The concept of MBL-VP has high potential for future implementation. The MBL-VP unit could be re-designed or modified to suit each case.

8.3 Part III: Membraneless-Vaporization Technique for Quantitative Analysis of Total Inorganic Arsenic by Hydride Generation and Chemiluminescence

The work on membraneless was extended for a new method development for determination of arsenic. Vaporization was this time by hydride generation like in the method for cold vapour atomic absorption. However we explored the use of chemicluminescence for this purpose. Use of chemiluminescence would allow for minituarization of the whole system. Selective analysis could be achieved from the hydride method and therefore this method is hoping to be an alternative to AAS.

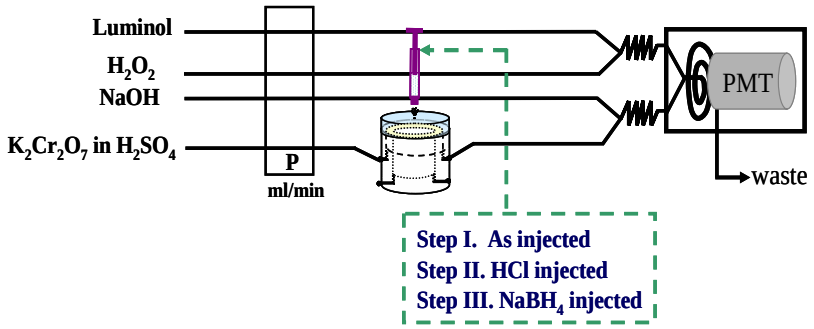

Fig. 8 A schematic diagram of MBL-PV system with chemiluminescence detection was investigated for arsenic measurement. Luminol: $8x10^{-4}$ M luminol in 0.1 M CO_3^{2-}, Oxidant: 0.01 M H_2O_2, NaOH: 0.5 M NaOH, Acceptor: 2 x 10^{-2} M $K_2Cr_2O_7$ (M) in 0.1 M H_2SO_4, $NaBH_4$: 0.5 %w/v $NaBH_4$, HCl: 2 M HCl, MBL-PV: membraneless-pervaporation unit, Detector: photomultiplier tube with a home-made flow cell.

8.3.1 Flow system with membraneless apparatus

The FI system with MBL-VP was designed as shown in Fig.8. By means of this system, hydride generation was occurred within the donor vial. All of the hydride generation reagents were injected directly by syringe through a hole at a middle of the lid. On the other hand, CL reagents as well as acceptor solution were propelled into a FI system by peristaltic pump. The flow system parameters that affect the sensitivity and reproducibility of the arsenic determination were studied separately according to their nature. A preliminary optimization of these parameters was investigated earlier in the normal FI system due to convenient and rapidity. The conditions used in the MBL-VP system are depicted in Fig.8. In the following topic,

only the influence of chemical concentrations for hydride generation on the analytical signal is described since they are affected by the physical of the donor vial (mixing geometry, evaporation rate and diffusion rate of the gas phase).

8.3.2 Optimization

In this work, we present a screening method for determination of total inorganic arsenic in environmental samples. The concentration of reagents for hydride generation was optimized in two form of arsenic, which were As(III) and As(V). In order to avoid error from difference form of inorganic arsenic, our criteria for the optimum condition was that the signal obtained from As(III) and As(V) must be equal.

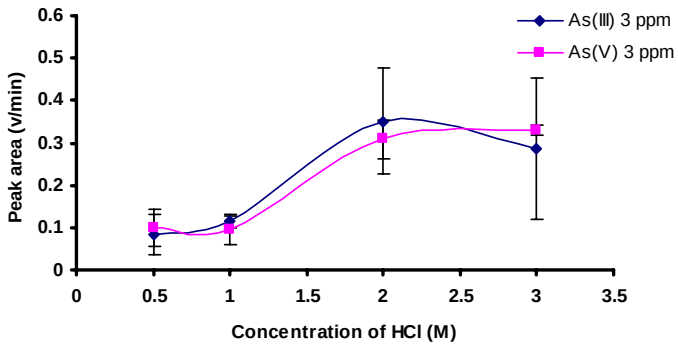

Fig.9 Effect of the concentration of HCl on the CL signal.

The effect of the HCl concentration on the arsine generation in the experimental MBL-VP system was investigated in the range of 0.5 to 3.0 mol l^{-1} when $NaHB_4$ concentration was fixed at 0.5 %(w/v). It was found that no difference between As(III) and As(V) was observed during the studied range, whereas the area of CL transient signal increased with increasing HCl concentration up to 2 mol l^{-1} after which the dependence level off (Fig.9). Note that the higher concentration of HCl, the greater deviation of the signals was obtained. For this reason, in all subsequent experiments 2 mol $l^{-1}$was used as optimum.

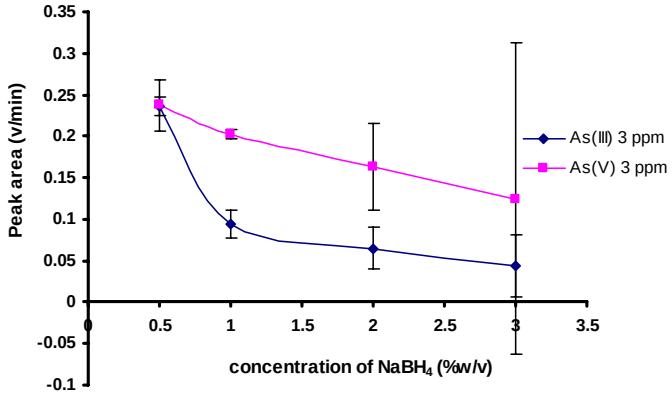

Fig.10 Effect of the concentration of $NaBH_4$ on the CL signal.

Various concentration of $NaBH_4$ were investigated in the range of 0.5 and 3.0 %(w/v). The measurement signal was found to decrease with increasing concentration of $NaBH_4$ (Fig.10). Moreover, a poor repeatability of the signals was observed when $NaBH_4$ concentration increased. This is due to an excessive bubble from H_2 gas occurred during the hydride generation step. Therefore, in this work, 0.5 %(w/v) of $NaBH_4$ was chosen because it provided greater signal size and better precision.

8.3.3. Analytical features

Under the optimized conditions, the calibration is always linear within the concentration range 1.0-10.0 mg /L.

An example of the calibration curve obtained from this work is $y = 0.085x - 0.026$ ($r^2 = 0.999$), when y is the peak area and x is the concentration of iodide injected. The precision of the flow injection method obtained for ten replicate injections of 3 mg /l was 4.8 %, expressed as relative standard deviation. The detection limit, defined as three times the standard deviation obtained from five replicate injections of blank signals, was 1 mg /l. The sample throughput, taking from injection of sample until the cycle of system operation is complete, was 7 injections per hour.

8.3.4. Application for water sample

The proposed method was applied to five river water samples. The samples were analyzed directly without filtration. Since the level of inorganic arsenic in the sample is lower than detection limit of the proposed method, the measurement was performed by adding standard arsenic at concentration of 2.5mg.l^{-1}. Table 5 shows percentage of recovery obtained from adding either As(III) or As(V) species. Average recovery of 103.4 and 101.6 % was obtained for As(III) and As(V), respectively. These results indicated that no interference was observed from these river water samples.

Table 5 Analytical recovery derived for determination of As(III) and As(V) in river water samples.

Water samples	Recovery (%) Added 5 mg l^{-1} As(III)	Recovery (%) Added 5 mg l^{-1} As(V)
W1	83.9	93.5
W2	95.7	92.6
W3	109.9	99.3
W4	115.8	114.6
W5	111.8	108

8.3.5. Application for soil and sediment and Interference study

The MBL-VP system was also used to determine arsenic concentration in more complicated matrices such as soil and sediment extracts. Validation of the method was done by analyzing arsenic content in contaminated area of Ron Piboon district in Nakhon Sri Thammarat province, Thailand using the proposed method and graphite furnace atomic absorption spectrometric (GFAAS) method. The results are presented in Table 6. By using regression test (Fig.11), it indicated that the MBL-VP-FI method provided higher value of arsenic contents compared to the GFAAS

Table 6 Arsenic content in soil and sediment sample extract determined by the MBL-VP and GFAAS method.

Sample	GFAAS (mg l^{-1})	SD	MBL (mg l^{-1})	SD
SE01_1	22.94	± 0.0006	31.04	± 0.0206
SE01_2	21.94	± 0.0015	29.69	± 0.0021
SE04_1	8.08	± 0.0006	11.33	± 0.0108
SE04_2	7.58	± 0.0025	8.40	± 0.0117
SE14_1	5.59	± 0.0020	12.88	± 0.0231
SE14_2	5.72	± 0.0028	10.10	± 0.0228
S03_1	2.68	± 0.0010	4.42	± 0.0061
S03_2	3.20	± 0.0012	4.85	± 0.0113

method. We surmise that the original positive error is due to the presence of metal ions in the sample matrix that interfere step of arsine generation.

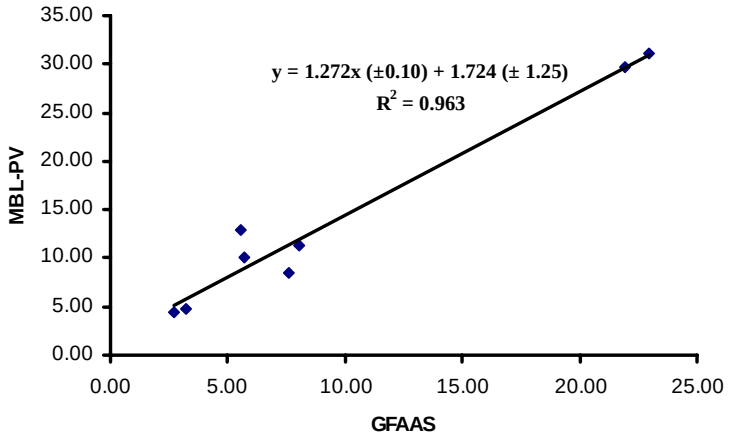

Fig.11 Regresstion plot between inorganic arsenic concentration of soil and sediment extracts obtained from the MBL-VP method and GFAAS method

To determine origin of this interference, we investigated the effects of individual metal ions that are present in sample extracts (previously measured in qualitative scanning mode in ICP-OES). Common metal ions such as aluminum, manganese, iron, tin and lead at various concentration were added separately into 5

mg l^{-1} of As(III) solution. It was found that these metal ions did not interfere at the concentration about two times of the normal level of those present in soil and sediment extracts. However, when a mixture of those metal ions was studied in the same way as individual test, the positive error at 30% was observed even at lower concentration used (Table 6). The evidence has shown that mixture of metal ions, interferes seriously in our method. Increasing in concentration of the hydride did not show any improvement in eliminating this kind of interfering effect. Other means of pretreatment is necessary for soil and sediment extracts that contain complicated matrices.

8.3.6 Conclusions for the work on use of membraneless for arsenic

We have used the membraneless-vaporization (MBL-VP) technique, which is a technique for vaporization of analyte or its derivative to improve selectivity, coupled with a chemiluminescence (CL) detection for arsine detection. This technique can be used as a screening method for assessing contamination of arsenic in environmental samples with no pretreatment step. The developed MBL-VP-FI system was successfully applied for the determination of arsenic in river water samples but significant signal alteration was observed in soil and sediment extracts.

8.4 Part IV: Necessity of membrane-based technique in the case of iodine

In the case of iodine analysis we have attempted to apply our newly developed technique for generation of iodine element (I_2) for vaporization of iodine vapour inside the second design of the membraneless unit. However, it was observed from preliminary results that it is not possible for the case of iodine generation. There was poor reproducibility which was due to the stickiness of iodine element after conversion from iodide ion in the donor stream. Since we used plastic (acrylic, PP, TEFLON as our flow path, this same polarity of iodine caused surface absorption onto the wall. Therefore we decided to break off our study with the membraneless for iodine. However that observation has led us into exploring this wall adsorption property by applying this with the technique of membrane-based analysis called pervaporation. The followings describe all the work that were carried out.

8.4.1 The PV-FI manifold

The FI system with a pervaporation unit is depicted in Fig. 12. An AS-90 series autosampler (Perkin Elmer, USA) was used for automatically loading of standard or sample solutions into the FI injection valve. A FIAS-300 module (Perkin Elmer, USA) was employed for pumping the reagents. A home-made pervaporation unit consisted of two circular Perspex blocks (61 mm diameter, 25 mm deep) held together by stainless steel ring clamps and four stainless steel bolts. Both the acceptor chamber (0.3 mm deep) and donor chamber (5.0 mm deep) were hexagonal in shape. PTFE membrane (40 mm diameter 1.5mm thickness; Trace Biotech AG, Germany) was used to separate the donor and acceptor chambers of the pervaporation unit. A home-made CL detector, used for monitoring the CL light from iodine-luminol reaction, consisted of a concentric spiral PFA (0.75 mm i.d., 100 cm length) flow cell fitted in front of the PMT (Oriel 7020 Photomultiplier, USA). PTFE tubing (0.75 mm. i.d.) was used for all manifold connections.

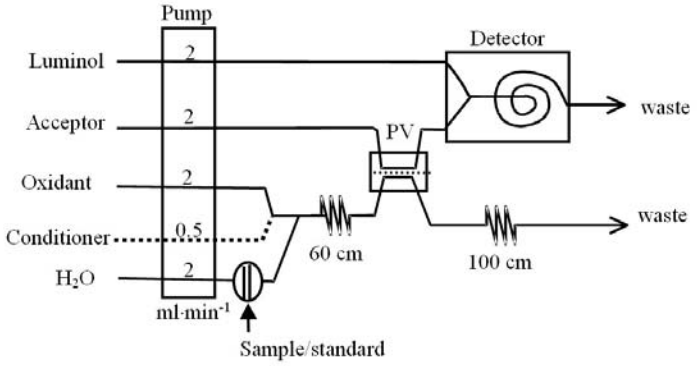

Fig.12 The employed PV-FI manifold. PV: pervaporation unit, Detector: photomultiplier tube with a home-made flow cell, Luminol: 7.5 x 10^{-4} M in 0.1 M NaOH, Acceptor: 1 % (w/v) KI , Oxidant: 0.01 M $K_2Cr_2O_7$ in 10% (v/v) H_2SO_4

8.4.2 Dual-detection FI for on-line detection of iodide and ascorbic acid after treated with anion exchange column

In this work, a dual-detection FI system coupled with an anion exchange resin column (Fig. 13), was used for optimization of the separation step between

ascorbic acid and iodide. A mixture of iodide and ascorbic acid solution was loaded onto the AER column, followed by pumping a solution of sodium nitrate, used as the eluent. The stream emerging from the column was split into two lines using a Y-connection tube. This allows for real-time monitoring of the elution of iodide and ascorbic acid. Within this dual-detection FI system, detection of ascorbic acid was based on reduction of potassium permanganate (Fig. 13). Detection of iodide was based on its catalytic effect on the redox reaction of Ce(IV)-As(III) (another system, see details in the published work), with a decrease in Ce(IV) concentration being monitored spectrometrically at 420 nm. Note that ascorbic acid was also detected by this redox reaction, since ascorbic acid also causes reduction of Ce(IV).

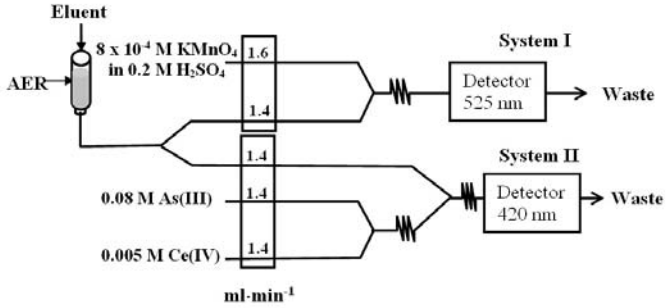

Fig.13 Dual–detection FI manifold for the optimization of the separation of ascorbic acid from iodide. Eluent: $NaNO_3$ solution, AER: anion exchange resin.

8.4.3. Manifold design and optimization

Our previous work using GD-FI system clearly demonstrated that molecular iodine was readily adsorbed onto the surface of the manifold tubing and the pores of the hydrophobic membrane. Without a conditioning stream of iodide solution (depicted as dashed line in the FI-Manifold shown in Fig. 12), signals within this range were not reproducible, and showed a gradual increase to reach a plateau as subsequent injections were made. With this background information, we used a similar FI system for PV, the manifold for which is shown in Fig. 12. The necessity for on-line conditioning system with continuous generation of iodine (I_2) was

investigated by varying the concentration of potassium iodide used in the conditioning stream (dashed line in Fig. 1) from 3 to 8 mg l^{-1}. The results presented

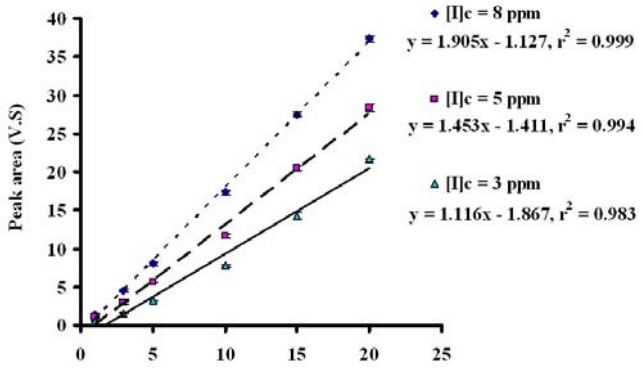

Fig.14 Calibration curves of the PV-FI obtained at three concentrations of the iodide conditioner or $[I]_c$ (3, 5 and 8 mg l^{-1}).

in Fig. 14, show that the linearity of calibration was not satisfied at 3 mg l^{-1}, whereas higher concentrations of 5 and 8 mg l^{-1} gave satisfactorily linear responses. Thus conditioning is also necessary for the pervaporation method, and a concentration of the conditioner at 5 mg l^{-1} was selected as the optimum condition for this purpose.
a decrease in peak area. Thus, 1% (w/v) KI was chosen as the acceptor solution.
The optimal concentrations of chemicals used in the preparation of reagent streams for the PV-FI system are listed in Table 7.

Table.7 Appropriate concentrations of the reagents used in the PV-FI system.

Reagent stream	Chemical (concentration unit)	Concentration value
Luminol	luminol (M)	7.5×10^{-4}
	NaOH (M)	0.1
Acceptor	KI (%,w/v)	1
Oxidant	$K_2Cr_2O_7$ (M)	0.01
	H_2SO_4 (%,v/v)	10
Conditioner	KI (mg l^{-1})	5

8.4.4 Analytical performance

Under the optimized conditions, the calibration was always linear within the concentration range 1.0-10.0 mg l^{-1}. A typical calibration equation curve obtained from this work is y = 2.319x – 1.1318 (r^2 = 0.999), where y is the peak area of CL signal and x is the concentration of iodide injected. A detection limit of 0.5 mg l^{-1} was determined (3 SD of the blank signal).

8.4.5 Application to iodide analysis of nuclear emergency tablets

Four samples of potassium iodide tablets, use for protection against thyroid absorption of radioactive iodine, were analyzed for iodide content using the developed PV systems. The iodide contents obtained from PV-FI system and ISE together with nominal values. The results were compared with the values accordingly to the labels. The contents of iodide, as determined by the PV-FI method, agreed significantly well with the labels. The paired *t*-test was employed to compare the difference in the results of KI tablets. No significant difference was found between the results from the PV-FI and from the ISE methods ($t_{observed}$ = 0.120, $t_{critical}$ = 3.18 at P = 0.05). This strong agreement demonstrated that the PV-FI method is suitable for analysis of samples of this type. It can be concluded that these pharmaceutical products do not exhibit any interference effects, since only dissolution of the KI tablets was employed before direct sample injection. Therefore the PV-FI system can be considered a viable alternative method to the GD-FI system and iodide electrode for iodide measurement in this type of sample.

8.4.6 Application to multivitamin tablets

From previous work performed using the GD-FI system, investigation of possible interfering species that are present in multivitamin extracts (i.e., vitamin B complex, vitamin C and some cations such as Mn^{2+}, Zn^{2+} and K^+ and anions such Cl^- and SO_4^{2-}) was carried out at concentrations that are twice the normal concentration. These substances did not exhibit a marked effect except for vitamin C which resulted in a

negative signal. For that reason, the interference of ascorbic acid was re-investigated in the developed PV-FI system. As expected, the same interfering effect was found. At higher concentrations of ascorbic acid greater negative signals were observed. Increasing the concentration of dichromate oxidant or even premixing sample with oxidant did not show any improvement in eliminating the interfering effect of ascorbic acid. Pre-treatment of sample extracts, by anion exchange separation, was therefore considered the most effective means of removing the ascorbic acid interference before injecting the multivitamin extracted into the FI system.

8.4.7. Method validation

Validation of the proposed method was done by analyzing iodide contents in 18 samples of multivitamin extracts using four different methods (PV-FI, GD-FI, ISE and ICP-MS). We found that sample matrix also interfere the iodide measurements by ISE method, resulting in negative error. Therefore, all the samples were pretreated using the described AER technique prior the analysis using the PV-FI, GD-FI and ISE. It was not necessary to use any type of clean up for the ICP-MS. Results for the comparison are presented in Fig. 15. The Analysis of Variance (ANOVA) test was used to compare the iodide content analyzed by the four methods. There was no significant difference between the results from the four methods at 95% confidence limit.

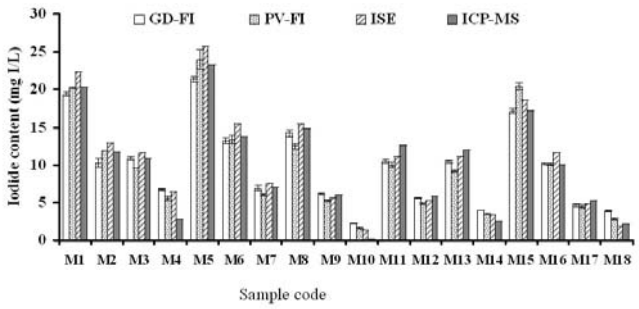

Fig.15 Comparison of iodide contents in multivitamin extracts determined by using four methods; GD-FI, PV-FI, ISE and ICP-MS.

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Outputs and Outcomes

Output จากโครงการวิจัย

สามารถแบ่ง outputs ที่ได้จากโครงการนี้เป็น 3 แบบ ดังนี้

1. ผลงานตีพิมพ์ในวารสารวิชาการนานาชาติ จำนวน 3 เรื่อง (และกำลังส่ง manuscript เพิ่มอีก 1 เรื่อง)

ได้แนบ reprints และ ร่าง manuscript มาพร้อมกับรายงานนี้

1.1 Choengchan N., Mantim T., Wilairat P., Dasgupta P.K., Motomizu S., and Nacapricha D. "A membraneless gas diffusion unit: design and its application to determination of ethanol in liquors by spectrometric flow injection", *Anal. Chim. Acta.*, 579 (2006) 33-37 (impact factor 3.186).

1.2 Nacapricha D., Sangkarn P., Karuwan C., Mantim T., Waiyawat W., Wilairat P., Cardwell T., McKelvie I. D., and Ratanawimarnwong N. "Pervaporation-flow injection with chemiluminescence detection for determination of iodide in multivitamin tablets", *Talanta*, 72 (2007) 626-633 (impact factor = 3.374).

1.3 Sereenonchai K., Saetear N., Amornthammarong N., Uraisin K., Wilairat P., Motomizu S. and Nacapricha D., "Membraneless vaporization unit for direct analysis of solid sample" *Anal. Chim. Acta.*, 597 (2007) 157-162 (impact factor 3.186).

1.4 Ratanawimarnwong N, Sangkarn P., Tiyapongpattana W., Waiyawat W. Uraisin K. and Nacapricha D. A membraneless-vaporization technique for quantitative analysis of total inorganic arsenic by hydride generation and chemiluminescence (manuscript in final preparation)

2. การนำผลงานวิจัยไปใช้ประโยชน์

2.1 **เชิงพาณิชย์** ทางนักวิจัยได้รับโจทย์เพิ่มเติมจากภาคเอกชน (บริษัท บางกอกไฮแลบ จำกัด เพื่อทดสอบนำหลักการ membraneless vaporization technique นี้ เพื่อการพัฒนาชุดเครื่องวัดภาคสนาม สำหรับวัดระดับหินปูนต่อไป

2.2 **เชิงสาธารณะ** มีเครือข่ายความร่วมมือกับนักวิจัยที่มีชื่อเสียงทาง flow-based ของประเทศญี่ปุ่น Prof. Dr. Shoji Motomizu, Okayama University

2.3 **เชิงวิชาการ**

2.3.1 มีการสร้างนักวิจัยใหม่ คือ ดร.นวลละออ รัตนวิมานวงศ์ และ ดร. ณัฐวุฒิ เชิงชั้น ซึ่งร่วมในโครงการวิจัยตั้งแต่รับทุนโครงการปริญญาเอกกาญจนาภิเษก และปัจจุบันเข้าบรรจุเป็นพนักงานมหาวิทยาลัย ตำแหน่งอาจารย์ ที่ มศว. ประสานมิตร (ดร. นวลละออ) และ สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง (ดร. ณัฐวุฒิ)

2.3.2 มีการนำผลงานวิจัยเพื่อใช้ในประวัติ เพื่อการสมัครรับทุนต่าง ๆ

-นางสาวฐิติรัตน์ แม้นทิม ได้ใช้ผลงานตีพิมพ์เพื่อเป็นผลงานวิชาการที่ได้ผ่านการพิจารณาให้ transfer จากหลักสูตรปริญญาโท ให้เข้าศึกษาในหลักสูตรปริญญาเอก ตลอดจนได้รับการพิจารณาอนุมัติให้ทุนการศึกษา คปก. อีกด้วย

-นางสาวพรจันทร์ สั่งการ ได้ใช้ผลงานตีพิมพ์เพื่อเป็นผลงานวิชาการประกอบการสมัครงานในตำแหน่งครู และการสมัครเข้าศึกษาต่อ ณ ประเทศญุ่ปุ่น

-รวมถึงการใช้ผลงานในประวัติการขอรับทุนต่าง ๆ โดย หัวหน้าโครงการและผู้ร่วมโครงการในอนาคต 5 ปี (เนื่องจากแหล่งทุนมักขอประวัติผลงานตีพิมพ์ย้อนหลัง 5 ปี)

3. อื่น ๆ ที่เกี่ยวข้อง

3.1 หัวหน้าโครงการได้รับเชิญเป็น Editorial Board

วารสารวิชาการ Talanta ซึ่งเป็นวารสารทางเคมีวิเคราะห์ ได้เชิญให้หัวหน้าโครงการอยู่ใน Editorial board เป็นเวลา 2 ปี (1 มกราคม 2550 ถึง 30 ธันวาคม 2551)

3.2 การนำผลงานเสนอในที่ประชุมวิชาการระดับนานาชาติ

3.2.1 The 9th Asian Conference on Analytical & The 39th Convention of The Korean Society of Analytical Sciences, 4-8 November 2007, Jeju Island. Korea.Title: Virtual membrane permeation for selectivity

3.2.2 International Conference on Flow Injection Analysis. 3-7 September 2007, Berlin, Germany Title: “Innovative design of membraneless vaporization units for direct and selective analysis of volatiles in liquid and solid sample”

3.3 การได้รับเชิญเป็น invited speaker

หัวหน้าโครงการ ได้รับเชิญให้เป็น Invited speaker ณ มหาวิทยาลัยคยุงนัม ประเทศเกาหลี ในงานครบรอบ 60 ปีของมหาวิทยาลัย The ‘60th Anniversary of Kyungnam University, South Korea and The 12th International Symposium on Advanced Technology and Applications’, 2007.

ภาคผนวก

Reprint ผลงานตีพิมพ์
จำนวน 3 เรื่อง

มีรายการ reprints ที่แนบมาดังนี้

[1] Choengchan N., Mantim T., Wilairat P., Dasgupta P.K., Motomizu S., and Nacapricha D. "A membraneless gas diffusion unit: design and its application to determination of ethanol in liquors by spectrometric flow injection", *Anal. Chim. Acta.*, 579 (2006) 33-37 (impact factor 3.186).

[2] Nacapricha D., Sangkarn P., Karuwan C., Mantim T., Waiyawat W., Wilairat P., Cardwell T., McKelvie I. D., and Ratanawimarnwong N. "Pervaporation-flow injection with chemiluminescence detection for determination of iodide in multivitamin tablets", *Talanta*, 72 (2007) 626-633 (impact factor = 3.384).

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