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Micro-evaporation electrolyte concentrator

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Abstract

The sensitivity of miniaturized chemical analysis systems depends most of the time on the obtainable detection limit. Concentrating the analyte prior to the detection system can enhance the detection limit. In this writing an analyte concentrator is presented that makes use of evaporation to increase the ion concentration of an electrolyte. The evaporation rate can be enhanced using forced convection. In order to control the evaporation rate a nitrogen flow is fed over a liquid channel covered with a hydrophobic vapor permeable membrane. Water vapor can pass through this membrane in contrast to water itself because of the hydrophobic nature of the membrane surface. An electrolyte conductivity detector is used to measure directly the concentration effect as a function of the nitrogen flow velocity. The influence of the convective nitrogen flow and the residence time of the analyte inside the concentrator are investigated in this paper. It is shown that the evaporation rate is enlarged with an increase in convective flow. The concentration effect is also enhanced when the residence time of the analyte inside the concentrator is increased. The higher concentration enhancement due to the longer residence time, however, results in an increase in water vapor present in the nitrogen flow. This results in a lower normalized evaporation rate when the available evaporation time is enlarged.

Keywords: Electrolyte solution concentrator; Micromachined membrane; Evaporator

1. Introduction

Lately, much research has been performed on the miniaturization of chemical analysis systems. A major issue in such systems is the obtainable detection limit. This paper presents a method to increase the concentration of dissolved small particles or ions by use of evaporation of the solvent. Macro-evaporation concentrators are used in the chemical and food industry, for instance in systems that remove water from streams like milk or fruit juices [1,2].

The evaporation rate of aqueous solutions is normally expressed as the decrease in mass of the solution per unit of time. This mass decrease, $\dot{m}$ (kg/h), depends on the diffusivity of water vapor into the surrounding air, D (m^2/h), the size of the exchange surface, A (m^2), and the difference between the saturation vapor pressure of the solution, at the liquid/gas interface, and the water vapor pressure of the surrounding gas, $\partial P/\partial x$ (mm Hg) [3]:

$$\dot{m} = -D_{AB} A \frac{\partial P}{\partial x} \tag{1}$$

Moreover, the evaporation rate is increased significantly when the diffusivity of the water vapor, away from the solution, is enlarged. This is accomplished by active removal of water vapor by convection [3]:

$$\dot{m} = -\bar{h}_D A \frac{\partial P}{\partial x} \tag{2}$$

The principle of evaporation is shown schematically in Fig. 1. The convective mass transfer coefficient, $\bar{h}_D$, is a function of the velocity of the airflow causing the convection.

In spite of the fact that the theoretical description of evaporation is readily available, calculating the evaporation rate of an evaporations system is not straightforward. Therefore, most of the literature about the evaporation rate, almost a countless number dating back to the late 1800s, focuses on empirical relations between air velocity and water evaporation [3–7]. Ref. [4] is a review on equations for the calculation of the evaporation rate. Many of the reviewed articles concern evaporation from swimming pools. Such measurements are mostly performed in pans, installed in wind tunnel experiments [6].

There are different approaches to construct a miniaturized evaporation concentrator. The relative evaporation rates found in pan experiments are not very high because of the small evaporation surface in relation to the water

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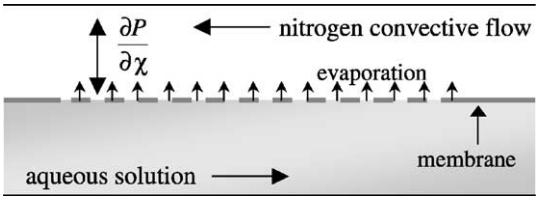

Fig. 1. Evaporation enhanced by a convective nitrogen flow.

volume. Such an approach is therefore not suitable for the construction of a miniaturized concentrator. A much higher surface/volume ratio is obtained in so-called thin film concentrators. Milk concentrators, for example, are constructed using this principle. In this case a falling thin film is created that is heated using steam [1].

An alternative to the thin film approach is the membrane evaporator. The latter offers the advantage of a constant surface/volume ratio. A second positive feature is the fact that there is a membrane between the analyte and the gas flow so that the analyte cannot be contaminated by particles in the gas flow. This evaporator approach is also the easiest approach to integrate in a miniature system [8]. The membrane evaporation principle has already been used for concentrating solutions, [9], and has been applied as the driving force for a micro pump [10].

2. Experimental

The membranes used in membrane evaporators must be permeable for water vapor, but they should be water repellent in order not to let the feed solution through. A very suitable membrane would be a micro-porous hydrophobic membrane, like commercially available Teflon® membrane. Fig. 2 shows a SEM picture of such a membrane and a contact angle measurement picture showing the hydrophobic nature of the material.

An evaporator is made comprising a Perspex substrate, with the micro-porous Teflon® membrane and an underlying feed channel, and a cover comprising a gas channel. An electrolyte conductivity sensor is placed at the outlet of channel containing the analyte.

In the proposed design of the micro-concentrator, a membrane separates a gas/vapor channel from a liquid channel. The feed liquid is pumped through the channel underneath the membrane. Water vapor can pass through the membrane into the gas channel where it is removed by a gas flow. The gas is pumped into the second channel in counter flow. In this way the vapor pressure difference at the membrane surface is maximal over the total length of the channel.

The concentration of a low concentration NaCl solution is measured prior to the concentration step. The ion concentration at the outlet of the system is measured to detect whether the ion concentration has increased. A schematic drawing of the described system is shown in Fig. 3.

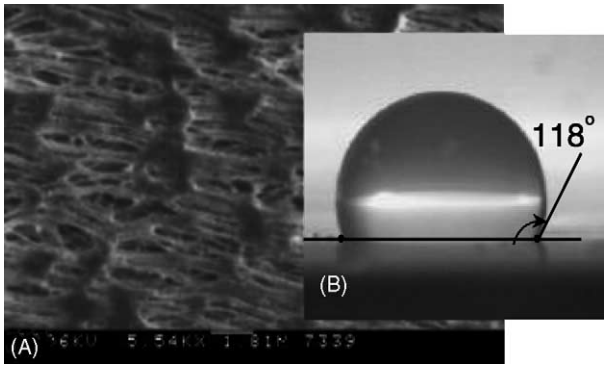

Fig. 2. Micro-porous Teflon® membrane image showing a SEM picture of the 0.2 μm holes (A) and a contact angle measurement showing the water repellency of the surface (B).

In Eq. (2) it is stated that to enhance evaporation, the air velocity can be increased (I), the membrane surface area can be enlarged (II) or the difference between the saturation water vapor pressure of the analyte and the water vapor pressure of the gas phase can be made as large as possible (III). The third option is commonly used and is fulfilled by raising the analyte temperature. Therefore, many applications work at an elevated temperature. However, for biomedical tests, heating of the analyte is not always applicable. On the other hand, it is possible to concentrate the analyte at room temperature. Using an inert, dried, gas as the convection gas, for instance nitrogen gas, can also satisfy a high vapor pressure difference.

Another option to enhance the concentration effect is to increase the concentration time, in order to let more water vapor be drained away. The influence of the gas flow velocity and the analyte flow on the concentration enhancement due to evaporation is investigated in this paper.

The liquid feed is a low concentration NaCl solution that is pushed into the system, using a CMA 102 microdialysis syringe pump. A low concentration is used because the system is designed to increase the sensitivity of analytical systems, where low ion concentrations have to be analyzed. The time available for evaporation depends on the flow of the analyte. Therefore, the pump velocity is a parameter for the amount of concentration enhancement.

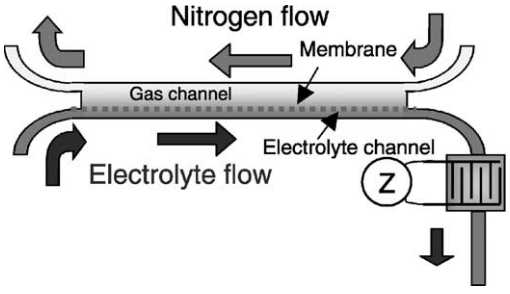

Fig. 3. Schematic diagram of the evaporation concentrator, comprising a gas channel, an electrolyte channel and an electrolyte conductivity (EC) sensor.

A specially designed electrolyte conductivity sensor for low ion concentrations [11] is integrated in the system to measure the ion concentration increase due to the evaporation. The sensor dimensions are 2 mm × 5 mm, resulting in an internal volume of 113 µl. An interdigitated electrode structure is used to lower the cell constant. This makes the sensor sensitive enough to measure very low electrolyte concentrations.

3. Results and discussion

The first concentration parameter that is investigated is convection, in the form of the flow velocity of a nitrogen flow. The concentration enhancement is determined as function of the velocity of a dried nitrogen flow, blowing over the analyte that flows through an underlying channel. An 83 µM NaCl solution, measured with the electrolyte conductivity detector, is pumped into the channel with an internal volume of 135 µl at a flow rate of 7.5 µl/min. The channel is covered with a Teflon® membrane with an estimated contact surface of 230 mm^2. The concentration of the analyte solution is measured at the outlet of the concentrator. Fig. 4 shows the concentration of the electrolyte measured as a function of nitrogen velocity over the membrane.

It is shown that the concentration can be increased without heating up the system by enhancing the convection factor. This is in correspondence with results found in literature, describing pan experiments.

In order to compare the found results with literature on evaporation, the mass decrease per hour is calculated as a function of the nitrogen velocity, normalized for the evaporation area and the vapor pressure difference between the analyte and the gas. Because dried nitrogen is used as convective gas a bulk water vapor pressure of zero is assumed for the gas flow. Fig. 5 shows the evaporation rate calculated from Fig. 4 and, in dashed lines, results from pan

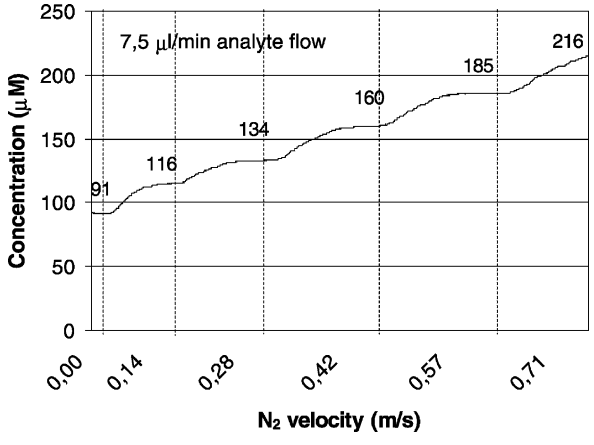

Fig. 4. Concentration at the outlet of the concentrator as a function of the nitrogen flow velocity. The initial NaCl concentration was 83 µM.

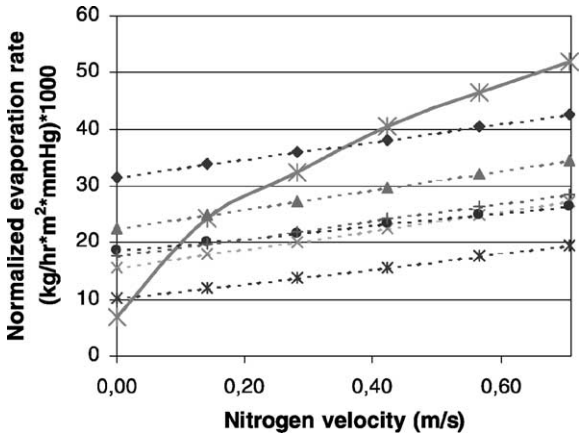

Fig. 5. Normalized evaporation rates as a function of the gas flow velocity at the liquid/gas interface. The dashed lines are taken from literature [5].

experiments conducted at different places in the world, summarized in a review article by Smith et al. [5].

When the convective mass transfer coefficient is increased, by accelerating the nitrogen flow velocity, the evaporation rate is enhanced. At the membrane there will be a water vapor film. The thickness of this film is dependent on the velocity of the gas flow. This means that faster removal of the water vapor at the membrane interface results in a thinner water vapor film and therefore in an enlargement of the amount of water that is removed form the analyte flow. This result was already described by Eq. (2).

Although it is not very clear from Fig. 5, there is quite some difference between evaporation rates found in experiments reported in literature. Especially at zero wind-velocity the differences are significant. For gas velocities approaching 0, the measured evaporation shown in Fig. 5 is lower, compared to the results found in other investigations. This can be explained by looking at the used experimental setup. The found evaporation curves are all measured in pan experiments where even at zero air velocity water vapor can diffuse into the air. In our case the gas flows through a channel. At zero gas velocity the vapor pressure inside the channel will saturate soon because there is only a small outlet where water vapor can diffuse out of the channel. The lower diffusion rate will reduce the evaporation rate, as shown in Eq. (1). At higher gas velocities the measured evaporation is higher than expected from literature.

A second evaporation parameter that is investigated is the time that is needed for the analyte to flow through the concentrator, the residence time. The analyte flow of a low NaCl concentration is varied between 5 and 25 µl/min. A nitrogen flow velocity of 0.14 m/s is applied. The concentration is measured again using the electrolyte concentration detector. The result of this experiment is shown in Fig. 6.

Fig. 6 shows that a reduction of the analyte flow in the evaporator does result in a higher concentration enhancement, as expected. From the internal volume, 135 µl, and

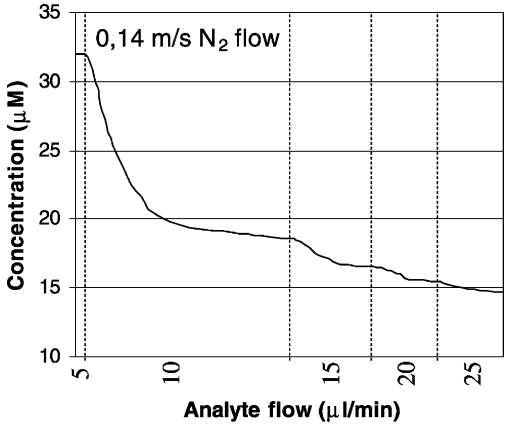

Fig. 6. Concentration at the outlet of the concentrator as a function of the analyte flow. The initial NaCl concentration was 11.1 μM.

the analyte flow, the residence time of the analyte inside the concentrator can be calculated. In order to determine whether the mass reduction caused by evaporation is time dependent, the normalized evaporation rate is calculated as a function of the residence time. This result is shown in Fig. 7.

When the residence time of the analyte is prolonged, the normalized evaporation rate decreases significantly. Although the nitrogen flow velocity at the interface is much higher than the analyte flow velocity, it seems the analyte flow has an influence on the normalized evaporation rate. When the analyte flows slowly underneath the membrane, more water vapor diffuses into the gas stream than at higher analyte flow rates. In the calculations resulting in Fig. 7, it is assumed that the water vapor pressure of the gas flow is very low compared to the water vapor pressure of the analyte flow. There is, however, a difference between the amounts of vapor in the gas flow at different analyte flow velocities. At the smaller residence times more water vapor is present in the boundary layer above the membrane, resulting in a higher evaporation rate. This might be explained by a regional concentration effect. At a low analyte flow much water will evaporate, resulting in a high ion concentration directly underneath the membrane. The high concentration will reduce the saturation water vapor pressure and therefore the vapor pressure gradient. This will limit the evaporation. Water will diffuse towards this layer but this will take some time.

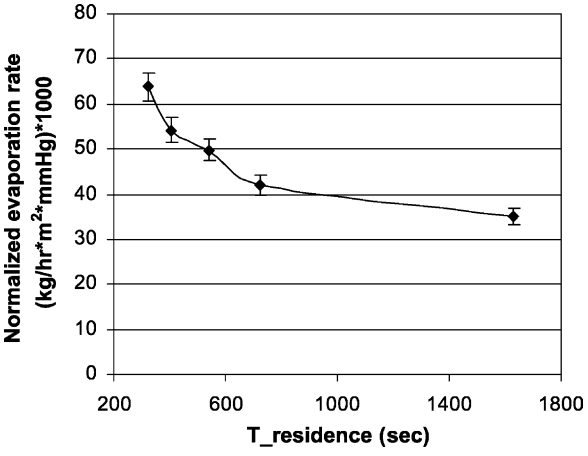

Fig. 7. Normalized evaporation rates as a function of the residence time of the analyte inside the concentrator.

4. Conclusions

An electrolyte concentrator for increasing analyte concentrations in order to improve the detection limit of analytical systems has been demonstrated. The concentrator is of the membrane evaporator type. The analyte is fed through a channel covered with a hydrophobic, vapor permeable, membrane. The concentration effect is enhanced by applying forced convection using a dried nitrogen flow over the membrane. The evaporation rate is shown to increase when the velocity of the nitrogen flow is raised. It is also shown that reducing the analyte flow results in a higher concentration effect but that there is a limit in reducing the analyte flow velocity. Not only will the system become very slow, also the normalized evaporation rate, describing the change in mass over time, will become lower. A threefold concentration effect has been demonstrated.

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Biographies

Bjorn Timmer was born in Nijverdal, the Netherlands, on December 25, 1975. He received the MSc degree in electrical engineering from the University of Twente, Enschede, the Netherlands, in 2000 on a micro dosing system for calibrating a miniaturized bed side monitoring system. He is now working as a PhD-student at the Biosensor Technology Group, The Lab-on-a-chip Group, of prof. Albert van den Berg. The subject of the PhD-project is the miniaturization of an ammonia detection system for trace amounts of ambient ammonia. The group is part of the MESA$^+$ Research Institute, of the University of Twente.

Koen van Delft was born in Laren, The Netherlands in 1978. He received a BSc in Precision Engineering, specialization Microsystem Technology, from the Hogeschool of Utrecht, the Netherlands, in 2001. Currently he is working as a technician at the Biosensor Technology Group, The Lab-on-a-chip Group. This group is part of the MESA$^+$ Research Institute, of The University of Twente.

Wouter Olthuis was born in Apeldoorn, the Netherlands, on October 23, 1960. He received the MSc degree in electrical engineering from the University of Twente, Enschede, the Netherlands in 1986 on the subject of thermally excited resonating silicon membrane pressure sensors. In that year, he joined the Center for MicroElectronics, Enschede (CME) doing research on inorganic electret materials for subminiature silicon microphones. In 1987 he started his PhD-project and received the PhD degree from the Biomedical Engineering Division of the Faculty of Electrical Engineering, University of Twente, in 1990. The subject of his dissertation was the use of Iridium oxide in ISFET-based coulometric sensor-actuator devices. Since 1991 he is working as an Assistant Professor in the Laboratory of Biosnesors, part of the MESA$^+$ Research Institute, of the University of Twente and as such co-supervising many projects on both physical and (bio)chemical sensors and sensor systems for medical and environmental applications.

Piet Bergveld was born in Oosterwolde, The Netherlands, on January 26, 1940. He received the MSc degree in electrical engineering from the University of Eindhoven, the Netherlands, in 1965 and the PhD degree from the University of Twente, the Netherlands, in 1973. The subject of his dissertation was the development of ISFETs and related devices. Since 1965 he has been a member of the Biomedical Engineering Division of the Faculty of Electrical Engineering (University of Twente) and was in 1984 appointed as Full Professor in Biosensor Technology. He is one of the project leads in the MESA$^+$ Research Institute. His research subjects still concern the further development of ISFETs and biosensors based on ISFET technology as well as physical sensors for biomedical and environmental applications, resulting up to now in more than 320 papers and 25 Theses. He was Research Dean from the Faculty of Electrical Engineering from 1994 to 1998 and received in 1995 the Jacob Kistemaker Award. He was founder and chairman of the international steering committee of the annual microTAS Symposia from 1994 to 2000. In 1997 he was appointed as a member of the Royal Dutch Academy of Sciences. He retired in 2003.

Albert van den Berg received his Masters degree in applied physics from the University of Twente, The Netherlands in 1983. In 1988 he finished his thesis at the same university on the topic of chemically modified ISFETs. From 1988 to 1990 he was at the Swiss Center for Microelectronics and Microtechnology (CSEM) in Neuchâtel, Switzerland, project manager in the chemical sensor department. From 1990–1993 he did research on miniaturized chemical sensors and sensor systems at the IMT, University of Neuchâtel, Switzerland. From 1993 until 1999 he was research coordinator Micro Total Analysis Systems (μTAS) at MESA, University of Twente, a topic that was recently extended to Miniaturized Chemical Systems (MiCS). In 1998 he was appointed as full professor on Miniaturized Systems for (Bio)Chemical Analysis at the faculty of Electrical Engineering. Since 2002 he is chair of the Lab-on-a-Chip group at the University of Twente. Dr. van den Berg is member of the μTAS steering committee and editor of the section μTAS of Sensors and Actuators B. His current research interests focus on theory, technologies, new devices and applications of micro- and nanofluidics for miniaturized (bio)chemical synthesis and analysis systems.