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Chelate titrations of Ca^{2+} and Mg^{2+} using microfluidic paper-based analytical devices

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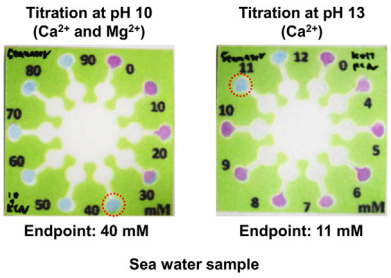
HIGHLIGHTS

- Novel μPADs for the determination of both Ca^{2+} and Mg^{2+} were developed.
- The μPAD titration is completed within a few minutes.
- The μPAD titration requires no particular skills as needed in the classic titrations.
- The method achieves low consumption of the reagents and samples.
- The μPADs can be employed for the determinations of practical samples.

GRAPHICAL ABSTRACT



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ABSTRACT

We developed microfluidic paper-based analytical devices (μPADs) for the chelate titrations of Ca^{2+} and Mg^{2+} in natural water. The μPAD consisted of ten reaction zones and ten detection zones connected through narrow channels to a sample zone located at the center. Buffer solutions with a pH of 10 or 13 were applied to all surfaces of the channels and zones. Different amounts of ethylenediaminetetraacetic acid (EDTA) were added to the reaction zones and a consistent amount of a metal indicator (Eriochrome Black T or Calcon) was added to the detection zones. The total concentrations of Ca^{2+} and Mg^{2+} (total hardness) in the water were measured using a μPAD containing a buffer solution with a pH of 10, whereas only Ca^{2+} was titrated using a μPAD prepared with a potassium hydroxide solution with a pH of 13. The μPADs permitted the determination of Ca^{2+} and Mg^{2+} in mineral water, river water, and seawater samples within only a few minutes using only the naked eye—no need of instruments.

1. Introduction

Since the first demonstration by Whitesides' group in 2007 [1], microfluidic paper-based analytical devices (μPADs) have gained a significant amount of attention as an analytical platform. Several publications have recognized μPADs that are fabricated from paper substrates as suitable for point-of-care testing and on-site analysis [2–4], because they are easy to fabricate, light, inexpensive, disposable, transportable, and instrument-free.

As seen in a recent review article on μPADs [5], several detection methods including colorimetry [6–8], electrochemistry [9–11], fluorometry [12], chemiluminescence [13,14], and electrochemiluminescence [15], have been reported in the past decade. Among them, colorimetry is the most popular detection scheme whereby a scanner or digital camera captures the color image of a μPAD, followed by a measurement of the color intensity using image-processing software [7,16–19]. For the purpose of point-of-care testing, smart phones are coupled with μPADs since smart

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phones are equipped with both a camera and image-processing software in a small package [20].

Conversely, the naked eye is a potentially excellent detector, as we demonstrated in a previous study on μPADs used for acid-base titrations [21]. Using the μPADs, the endpoint of the neutralization reaction can be visualized by a color change in the detection zone adjacent to the reaction zone containing an equivalent amount of titrant. The first attempt at using the naked eye was in distance-based detection, which was developed by Henry's group [22]. The length-based detection scheme permitted the determinations of glucose, glutathione, nickel ion [22], and lactoferrin [23]. With these methods, the concentration of an analyte was determined by the length of the colored channel that became elongated with increases in its concentration.

In our previous research, we demonstrated acid-base titrations on μPADs consisting of ten reaction zones and ten detection zones [21]. Strong and weak acids and bases could be titrated by selecting an appropriate indicator. The principle would obviously be applicable to other classic titration methods that include chelate titrations, redox titrations, and precipitation titrations. Although the detection scheme is slightly different, iodometry was demonstrated as an example of redox titrations [24]. In addition, acid-base titrations were achieved using another type of paper-based device, which was constructed by stacking two conventional PADs on top of one another and bonding them together [25]. As seen in these articles, μPAD-based titrations are expected to be an alternative to classic titration techniques since they simplify the operations, reduce consumption of the reagents, facilitate on-site analysis, and are free from treatment of waste solutions after titrations due to possible incineration disposal.

In the present study, we developed μPADs for chelate titrations of Ca^{2+} and Mg^{2+} using ethylenediaminetetraacetic acid (EDTA) according to the same principle as that previously reported for acid-base titrations. Several factors including selection of the buffer components and the indicator, amounts of chemicals added to the μPAD, and the channel length were optimized to obtain accurate and precise analytical results. The developed μPADs were successfully applied to the rapid determinations of Ca^{2+} and Mg^{2+} in mineral water, river water, and seawater samples.

2. Experimental

2.1. Chemicals

Deionized water was prepared by means of an Elix water purification system (Millipore Co. Ltd., Molsheim, France). N-Cyclohexyl-3-aminopropanesulfonic acid (CAPS) was obtained from Dojindo Molecular Technologies, Inc. (Kumamoto, Japan). Magnesium sulfate, calcium chloride dihydrate, sodium hydroxide, iron(III) standard solution (1000 ppm), 1-(2-hydroxy-1-naphthylazo)-2-naphthol-4-sulfonic acid sodium salt (Calcon), and 2-hydroxy-1-(2-hydroxy-4-sulfo-1-naphthylazo)-3-naphthoic acid (NN) were purchased from Wako Pure Chemical Industries (Osaka, Japan). Ammonium chloride, ammonium hydroxide solution, potassium cyanide, and Eriochrome Black T (EBT) were obtained from Kanto Chemical (Tokyo, Japan). Ethylenediaminetetraacetic acid, disodium salt (EDTA· 2Na) and methanol were purchased from Sigma–Aldrich (St. Louis, MO, USA). All indicators were dissolved in methanol at a concentration of 0.1 (w/v)%. A buffer solution with a pH of 10 was prepared by dissolving appropriate amounts of CAPS in water and adjusting the pH with a sodium hydroxide solution.

2.2. Fabrication and preparation of the μPADs

The structure of the μPAD employed in this study was similar to that reported previously [21] except for the channel length between the reaction and detection zones (Supplementary Material, Fig. S1). Microsoft Office Power Point 2010 was used to design the μPADs with a sample zone located at the center and ten reaction and detection zones each arranged radially in a 30 × 30 mm square. According to a method developed by Carrilho and co-workers, the designed μPADs were printed on a sheet of filter paper (200 × 200 mm, Chromatography Paper 1CHR, Whatman, GE Healthcare Lifesciences, United Kingdom) using a wax printer (ColorQube 8570DN, Xerox, CT, USA) [26] followed by heating at 120 °C for 3 min in a drying machine (ONW-300S, AS ONE Corporation, Osaka, Japan). The back of the printing surface was covered with transparent packing tape to prevent solutions from leaking from beneath the μPAD.

Each μPAD was cut into a piece that measured 30 × 30 mm, and then 30 μL of the buffer solution (pH 10 or 13) was added to the sample zone so as to completely fill the surfaces of the channels and zones of the μPAD (30 μL is the volume needed to fill all hydrophilic channels and zones [21]). The μPAD was completely dried, and then a 1 μL solution of ten different EDTA concentrations was added to each of the reaction zones since the volume needed to fill a reaction zone was determined to be 1 μL as reported in the previous paper [21], and 0.5 μL of a 0.1 (w/v)% indicator solution was added to each of the detection zones. To accomplish titration, the μPAD was placed on an acrylic plate holder that was composed of two 30 × 30 mm plates with four fins at the corners of the holder in order to avoid bending of the μPAD (Supplementary Material, Fig. S1). Finally, a micropipette was used to introduce 30 μL of the sample solution from the center of the μPAD.

2.3. Principle of chelate titrations using the μPADs

The principle of chelate titrations is similar to that of classic chelate titrations for Ca^{2+} and Mg^{2+} with EDTA, wherein the total concentration is determined at pH 10, whereas only Ca^{2+} is titrated at pH 13 since Mg^{2+} is masked with hydroxide ion so as not to react with EDTA [27]. However, in contrast to the classic titrations, the concentrations of Ca^{2+} and Mg^{2+} are directly determined by finding the endpoint from the color change without either calibration or calculation when using the μPAD method. When a sample solution is introduced into the center of the μPAD, the sample solution penetrates into ten reaction zones. Then, 1 μL of the sample solution can react with EDTA at each reaction zone since the volume occupying the reaction zone is 1 μL, which is the same as the volume of EDTA solutions added to the reaction zones. So, when the amount of metal ions exceeds that of the EDTA in the reaction zones, uncomplexed metal ions penetrate the detection zones, resulting in a color reaction of blue (free form) to purple (complex with metal ion) from the indicator. The concentration of the metal ion is equivalent to the lowest EDTA concentration of the reaction zone among those adjacent to the detection zones with blue color, which indicates no influx of the uncomplexed metal ions. Therefore, in the proposed method, we need to know only the exact concentrations of EDTA added to the reaction zones without further calibration.

2.4. Practical samples

Bottles of commercially available mineral water were purchased at a local supermarket. Natural water samples were taken from the Asahigawa River, from Kojima Bay, and from the Shimotsui Fishery Harbor in Okayama Prefecture, Japan. The sample solutions were kept in plastic bottles and were determined in our laboratory. The