**Research Article** 

# Liquid marbles as microreactors for qualitative and quantitative inorganic analyses



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#### Abstract

Conventional qualitative analysis of ions from inorganic salts and acid–base and redox titrations require relatively large volumes of solution and hence require more reagent and generate relatively large amount of waste. Liquid marbles can be used to cut down the volume of solution and by extension the amount of reagent and volume of waste generated. Liquid marbles were used for qualitative analysis of ions from inorganic salt solutions and acid–base and redox titrations. This was compared with the conventional methods which require milliliters of solution. Fumed silica or fluorinated sericite clay particles of varying degrees of hydrophobicity were used to prepare the marbles. A drop of a test reagent was then placed on the marble, merging with it and initiating a chemical reaction. The characteristic reactions between a salt solution and a test reagent in the marbles were observed provided the reaction was clearly marked by a color change. Concentrations, calculated from the volume at the end-point, compared closely ( $p \le 0.05$ ) with the known ones as well as those calculated from the bulk titration method that requires milliliters of solution. This indicates that the liquid marble method which rather requires microliters of solutions is reliable. These findings are especially important in microfluidics which utilizes microliters of solutions.

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#### **Graphic abstract**



**Keywords** Liquid marbles · Microreactor · Qualitative analysis · Quantitative analysis · Titration · Solution standardization

### 1 Introduction

Following their first report [1], various applications of liquid marbles-millimeter-size particle-coated liquid drops [2]—have emerged. Liquid marbles have been used to transport relatively small amounts of water, using gravitational, magnetic or electric fields from one point to another without leakage [3]. The coating of a liquid drop with powdered particles changes the liquid-substrate (solid) contact to a solid-solid contact, reducing viscous drag and allowing quick motion and preservation of the encased liquid drop. In another study [4], aqueous liquid drops (5–70  $\mu$ L) were loaded with  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> particles and coated with polyvinylidene fluoride particles and used as ferrofluidic bearings for the fabrication of a magnetic fieldactuated microfluidic device. The particle shell encasing the liquid drop is permeable to gas and can be used for gas sensing in environmental science [5, 6]. On this basis, marbles of phenolphthalein and CuCl<sub>2</sub>·2H<sub>2</sub>O or CoCl<sub>2</sub>·2H<sub>2</sub>O solutions, stabilized by polytetrafluoroethylene particles, were exposed to NH<sub>3</sub> vapor from ammonia solution where a rapid color change was noticed [5, 6]. This was immediately applied in the printing industry to sense NH<sub>3</sub> gas, which is released during the printing process [6]. Liquid marbles can float depending on the surface free energy of the particles encasing the liquid drop, the surface tension and pH of the bulk liquid. Poly(2-vinylpyridine)-stabilized

SN Applied Sciences A Springer Nature journal aqueous marbles disintegrate in solutions with pH < 2.9, but remain intact at higher values and can be used for the qualitative check of aqueous solution pH [7]. Similarly, polyvinylidene fluoride-stabilized aqueous marbles float stably on uncontaminated water, but disintegrated once contaminated with silicone oil and kerosene and hence can be used for detecting water contaminated with oil in the case of oil pollution [8]. A pressure difference exists between equivolume marbles, stabilized by different particles, and marbles of different volumes such that materials flow from the marble of higher pressure to the one of lower pressure when connected by a capillary tube until the pressures equilibrate [9]. Thus, marbles can be used as micropumps or for designing microreactors where the delivery of relatively small volumes of liquid is required [9]. It is easy to load substances into liquid marbles especially with a needle and syringe. This property has been utilized in human blood typing where the marble serves as a micro-bioreactor [10]. This requires a relatively small amount of sample and reagents and reduces biohazard risks. Blood samples (30 µL) were encapsulated with polytetrafluoroethylene or calcium carbonate particles which were treated with stearic acid. Antibody solutions (Anti-A, B, and D) were injected into the marbles and observed for the haemagglutination reaction under bright light [10]. Gases flow in and out across the particle layer encapsulating a marble such that it is possible to cultivate

microorganisms and cells. To demonstrate this, aqueous liquid drops (20 µL) were coated with polytetrafluoroethylene particles and injected with cultures of anaerobic *Lactococcus lactis cremoris* and aerobic *Saccharomyces cerevisiae* and incubated at 30 °C for 24 h [11]. There was rapid proliferation of *S. cerevisiae* cells which require oxygen to thrive as opposed to the *L. cremoris* ones which do not necessarily require oxygen. In line with this, marbles have been used to produce 3-D cell structures like cancer cell spheroids necessary for studying their physiology [12]. The use of liquid marbles in drug screening has also been demonstrated [13]. Liquid marbles are precursor of novel materials like the so-called powdered liquids [14, 15] and powdered emulsions [16, 17].

Liquid marbles have also been utilized in miniaturized chemical processes which require microliter volumes of reagents. Miniaturized chemical processes have several advantages. For example, they are cheaper, faster, less hazardous and generate less waste compared with their macroscale analogues. In addition, they are important in highthroughput analyses as well as purification processes like drug discovery, DNA analysis, protein crystallization and molecular synthesis [2]. Their small volume, non-wetting tendency and ease of manipulation via gravity, electric or magnetic fields [18] make liquid marbles suitable candidates for miniaturized chemical processes. For instance, the reaction between KI and AgNO<sub>3</sub> that forms AgI crystals has been miniaturized using marbles of KI and AgNO<sub>3</sub> solutions, stabilized by magnetic particles. The marbles were forced to coalesce using a magnetic field, initiating the reaction to give Agl precipitates [19]. Similarly, using a magnetic field, liquid marbles stabilized by magnetic particles containing H<sub>2</sub>O<sub>2</sub>, bis(2,4,6-trichlorophenyl)oxalate and a dye were coalesced to initiate a chemiluminescence reaction [20]. Other chemiluminescence reactions were performed with bicomponent marbles (containing different liquid types, e.g. water-in-oil or oil-in-water) stabilized by magnetic particles, containing the active ingredients in an immiscible liquid phase [20]. The marbles move in the presence of a magnetic field where the liquid drops coalesce to initiate the reaction [20]. Photochemical and acid-base reactions were also performed [20]. In another experiment [21], cyclohexane marbles (loaded with sebacoyl chloride) and aqueous marbles (loaded with hexamethylene diamine), stabilized by fluorinated fumed silica or fluorinated sericite particles, were coalesced mechanically to initiate the so-called nylon-rope reaction leading to the formation of Nylon 6-10. On the basis of miniature liquid marbles, Janus nanoparticles have also been synthesized [22, 23] and micro-electrochemical reactors have been fabricated [24]. The oxidation of an organic substrate, e.g. malonic acid by bromate ions in acidic medium in the presence of a single-electron transfer metal ion redox catalyst like ferroin, typically known as Belousov–Zhabotinsky reaction [25], has also been reported [26, 27] in liquid marbles.

Liquid marbles can also be used to perform simple qualitative analysis to identify cations and anions as well as perform simple quantitative acid-base reactions. However, this is yet to be demonstrated as far as we are aware. The work of Dorvee et al. [19] reported the precipitation of Agl from the coalescence of marbles of AqNO<sub>3</sub> and KI solutions under a magnetic field that can be used as the basis for qualitative analysis of Aq<sup>+</sup>. Similarly, acid-base reactions were reported in liquid marbles from the coalescence of a base and an acid marble under a magnetic field [20]. The aim of this work is to show that liquid marbles can serve as microreactors for simple qualitative analyses to identify inorganic cations and anions as well as perform quantitative acid-base reactions, which often involve relatively large volumes of reagents. Unlike previous work [19, 20] that require a magnetic field to coalesce the marbles, our approach does not require any force field for marbles coalescence. The required volume of a test reagent solution is released from a micro-pipette onto the marble where they coalesce to initiate a chemical reaction. Additionally, no end-point and quantitative results were reported in [20], raising the question of reliability in comparison to conventional methods. Thus, we further show that quantitative results obtained from the liquid marble approach agree closely with conventional methods that require large volumes of reagent solutions, supporting the suitability of liquid marbles as microreactors for these analyses. This can further be compared with microfluidic lab-on-a-chip devices [28], which are reaction-specific and require microchannels and external pumps to facilitate the manipulation of small amount of liquids. Although such devices have been modified to work without microchannels [29], sample contamination is still a major concern.

## 2 Experimental

#### 2.1 Materials

#### 2.1.1 Particles

Silica and sericite clay particles of varying degrees of hydrophobicity were used. A total of five silica particle types were used. The particles were hydrophobic Aerosil R202 and fumed silica containing 14, 33, 50 and 61% residual SiOH groups, which were obtained by chemical modification of the hydrophilic particles possessing 100% SiOH (N20, surface area = 200 m<sup>2</sup> g<sup>-1</sup>) using dichlorodimethylsilane. Aerosil R202 particles were a gift from Ramsamy Leon of Evonik Africa (Pty) Limited while the fumed silica particles were from Wacker Chemie, Germany. The hydrophobicity of the particles is related to the percentage of residual SiOH groups with particles having 14% SiOH being most hydrophobic while those with 61% SiOH being least hydrophobic [30, 31]. Three clay sericite particle types were used. The particles were PF-5, PF-8 and PF-12 fluorinated sericite clay particles from Daito Kasei Kogyo Company Limited, Japan. The particles are products of the surface chemical modification of their raw hydrophilic counterpart (PF-0) using varying amounts of C<sub>9</sub>-C<sub>15</sub> perfluoroalkyl phosphate diethanolamine salt such that PF-5 is the least hydrophobic while PF-12 is the most hydrophobic [15]. Further information about the fluorinated sericite clay particles can be obtained from Binks et al. [15] who used the particles for the preparation of oil marbles, dry oil powders, and oil foams.

### 2.1.2 Chemical reagents

Various acids, bases, salts and other reagents were used for the experiment. The source and purity of these reagents are given in Table 1. The salts were used in qualitative analysis while the acids and bases were used in acid–base titrations.

## 2.2 Methods

#### 2.2.1 Scanning electron microscopy of particles

The particles were viewed with a Ziess EVO 60 scanning electron microscope (SEM). A self-adhesive was applied

Table 1	Source and	purity of	chemical	reagents used
Tuble I	Source and	panty or	circinicai	reagenes asea

Reagent	Source	Purity/%
NaOH	BDH Chemicals Ltd	98
NH₄OH	May and Baker Ltd	25
HCI	May and Baker Ltd	36
HNO <sub>3</sub>	BDH Chemicals Ltd	70
H <sub>2</sub> SO <sub>4</sub>	May and Baker Ltd	96
lodine crystals	Burgoyne Urbidges and Company	99.5
КІ	Sigma-Aldrich	99.9
CaCl <sub>2</sub>	BDH Chemicals Ltd	95
Pb(NO <sub>3</sub> ) <sub>2</sub>	Pure Chemicals Ltd	99
PbS	BDH Chemicals Ltd	99
PbCO <sub>3</sub>	Fischer Scientific Company	98
CuSO₄·5H₂O	BDH Chemicals Ltd	98
FeCl₃·6H₂O	BDH Chemicals Ltd	98
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ·5H <sub>2</sub> O	BDH Chemicals Ltd	99
AgNO <sub>3</sub>	BDH Chemicals Ltd	99.9
ZnCl <sub>2</sub>	BDH Chemicals Ltd	99
Na <sub>2</sub> CO <sub>3</sub>	BDH Chemicals Ltd	70.6

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on a carbon sticky disk. The disk was then pressed into the powdered particles. Compressed air was blown over the disk to remove loosely held particles, leaving the tightly held ones which were then coated with a layer (~ 15 nm) of carbon using an Edward high vacuum coating unit. The particles were then exposed to an electron beam of voltage 20 kV and current 70 pA to obtain micrographs (Fig. 1) of the particles.

As evidenced from the SEM micrographs, individual silica particles (diameter 20–30 nm) fuse into quasi-spherical aggregates (several µm) irrespective of their %SiOH. Contrarily, individual sericite clay particles are platelets,  $\ge 2 \ \mu m$  long and a few nanometers thick and aggregated. The raw hydrophilic ones are relatively smooth compared with the fluorinated ones which are textured, perhaps due to Al(OH)<sub>3</sub> crystals used to augment the fluorination reaction [15].

## 2.2.2 Qualitative analysis

Many gualitative inorganic analyses involve at least two steps—a preliminary and a confirmatory step. Both steps normally require reacting bulk solutions (~ 2 cm<sup>3</sup>) of the unknown salt solution with drops and excess of the test reagents. On this basis, cations and anions from various bulk (~ 2 cm<sup>3</sup>) salt solutions were analyzed qualitatively and compared with the liquid marble approach. For cations (Table 2), test-tubes containing 2 cm<sup>3</sup> solutions (1 M) of CuSO<sub>4</sub>·5H<sub>2</sub>O, FeCl<sub>3</sub>·6H<sub>2</sub>O, ZnCl<sub>2</sub>, Pb(NO<sub>3</sub>)<sub>2</sub> and CaCl<sub>2</sub> were reacted with drops or excess NaOH or NH<sub>4</sub>OH solution (0.6 M). The test-tubes were then observed for characteristic reactions (Table S-1) that indicate the presence of Cu<sup>2+</sup>, Fe<sup>3+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup> and Ca<sup>2+</sup> ions, respectively. Similarly, test-tubes containing solutions (1 M) of Na<sub>2</sub>SO<sub>4</sub> and CaCl<sub>2</sub> were reacted with various test reagents (0.6 M) in drops and in excess (Table 3), and observed for characteristic reactions (Table S-2) that indicate the presence of  $SO_4^{2-}$ and Cl<sup>-</sup>, respectively.

In comparison, liquid marbles (40  $\mu$ L) of the various salt solutions were reacted with various solutions (10–25  $\mu$ L) of the test reagents and observed for the characteristic reactions. The volumes of the salt solutions used are in line with the maximum critical volume (100  $\mu$ L), above which the liquid marble collapses, determined prior to the experiment. To obtain a marble, a drop (40  $\mu$ L) of a salt solution was deposited from an Eppendorf micropipette onto a Teflon substrate (4 cm × 4 cm × 3 mm, Radio Spares, UK) containing a bed (100 mg) of the required powdered particles. The drop was rolled back and forth on the particle bed where the particles self-adsorb onto the drop surfaces giving rise to a marble [21], which was transferred

Fig. 1 (Upper) SEM micrographs of fumed silica particle powder containing **a** 100%, **b** 61%, **c** 50%, **d** 33% and **e** 14% residual SiOH groups and **f** Aerosil R202 powder. (Lower) SEM micrographs of: **a** raw hydrophilic (PF-0) and **b** PF-5, **c** PF-8, and **b** PF-12 fluorinated sericite clay particles





to a wider Teflon substrate (4 cm  $\times$  9 cm) for qualitative analysis (Fig. 2).

#### 2.2.3 Quantitative analysis

Acid (HCl, HNO<sub>3</sub> or H<sub>2</sub>SO<sub>4</sub>) solutions of known concentrations (0.2 or 0.6 M) were standardized by titrating against base (NaOH or Na<sub>2</sub>CO<sub>3</sub>) solutions of known concentrations (0.6 or 0.2 M) using suitable indicators. The required volume (25 cm<sup>3</sup>) of a base solution was measured into a conical flask and titrated against an acid solution in the presence of a suitable indicator (methyl orange or phenolphthalein) to the end-point marked by a color change. Using a combination of the volume of acid at the end-point, the volume of base and its concentration and the balanced equation of reaction (Table S-3), the concentration of the acid solution was calculated and compared with the known value. An average of three values is reported with the standard deviation for each acid–base system considered. For the liquid marble method, water was added to an aqueous liquid marble (20  $\mu$ L) at an increment of 5  $\mu$ L until it collapses at a maximum critical volume (100  $\mu$ L). Noting the maximum critical volume, liquid marbles (20–30  $\mu$ L) of the base solutions, containing drops of a suitable indicator, were prepared on a Teflon substrate and transferred to a wider Teflon substrate as described previously. Acid solutions (10  $\mu$ L) were added to the separate base liquid marbles using an Eppendorf micropipette

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Salt solution	Test reagent	Observation	Inference
CuSO <sub>4</sub> (aq)	(i) NaOH(aq) drops	Blue precipitate	Cu <sup>2+</sup> present
	NaOH(aq) excess	Blue precipitate (insoluble)	Cu <sup>2+</sup> present
	(ii) NH <sub>4</sub> OH(aq) drops	Deep blue precipitate	Cu <sup>2+</sup> present
	NH <sub>4</sub> OH(aq) excess	Precipitate dissolves (blue solution)	Cu <sup>2+</sup> present (confirmed)
FeCl <sub>3</sub> (aq)	NaOH(aq) drops	Brown precipitate	Fe <sup>3+</sup> present
	NaOH(aq) excess	Brown precipitate (insoluble)	Fe <sup>3+</sup> present (confirmed)
ZnCl <sub>2</sub> (aq)	(i) NaOH(aq) drops	White precipitate	Zn <sup>2+</sup> present
	NaOH(aq) excess	Precipitate dissolves (colorless solution)	Zn <sup>2+</sup> present
	(ii) NH <sub>4</sub> OH(aq) drops	White precipitate	Zn <sup>2+</sup> present
	NH <sub>4</sub> OH(aq) excess	Precipitate dissolves (colorless solution)	Zn <sup>2+</sup> present (confirmed)
Pb(NO <sub>3</sub> ) <sub>2</sub> (aq)	(i) NaOH(aq) drops	White precipitate	Pb <sup>2+</sup> present
	NaOH(aq) excess	Precipitate dissolves (colorless solution)	Pb <sup>2+</sup> present
	(ii) NH <sub>4</sub> OH(aq) drops	White precipitate	Pb <sup>2+</sup> present
	NH <sub>4</sub> OH(aq) excess	White precipitate (insoluble)	Pb <sup>2+</sup> present (confirmed)
CaCl <sub>2</sub> (aq)	NaOH(aq) drops	White precipitate	Ca <sup>2+</sup> present
	NaOH(aq) excess	White precipitate (insoluble)	Ca <sup>2+</sup> present (confirmed)

Table 3Observations andinferences for reactions ofsalt solutions (0.6 M) with testreagents (0.6 M) for qualitativeanalysis of anions

Salt solution	Test reagent	Observation	Inference
Na <sub>2</sub> SO <sub>4</sub> (aq)	(i) Dilute HCl(aq) drops	White precipitate	$S\Omega^{2-}$ present
CaCl <sub>2</sub> (ag)	(ii) + Excess dilute HCl(aq) (i) HNO₂(aq) drops	White precipitate (insoluble)	$SO_4^2$ present (confirmed)
2. 1	+ AgNO <sub>3</sub> (aq) drops (ii) + Excess dilute AgNO <sub>3</sub> (aq)	White precipitate White precipitate (insoluble)	Cl <sup>–</sup> present Cl <sup>–</sup> present (confirmed)

Fig. 2 Schematics of qualitative analysis in a liquid marble: **a** a drop of aqueous solution is rolled on a powdered bed of particles on a Teflon substrate, leading to liquid marble formation, **b** marble transferred to another Teflon substrate where drops of a test reagent solution are added, and **c** characteristic reaction occurs and marble changes color



in increments of 5  $\mu$ L to the end-point marked by a change in color of the marble. Similarly, a combination of the volume of acid at the end-point, volume of marble and its concentration and a balanced equation of the reaction (Table S-3) were used to calculate the concentration of the acid solution. This was compared with the known concentration and that from the previous experiment using milliliter volumes of solution. An average of three values is reported with the standard deviation for each acid–base system investigated.

In another experiment, iodine solution (0.6 or 0.2 M) was titrated against 25 cm<sup>3</sup> Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution (0.6 M) in the presence of starch to the end-point and the volume of iodine solution at end-point was similarly used to calculate its concentration and compared with the known concentration. Liquid marbles (20-30 µL) of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution containing starch were prepared on a Teflon substrate and transferred to a wider Teflon substrate as described previously. Starting with 10 µL, iodine solution was added to the separate Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> marbles using an Eppendorf micropipette in increments of 5 µL, to the end-point marked by a change in color of the marble. The volume of iodine at the end-point, in combination with the volume of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> marble and its concentration and the balanced equation of the reaction (Table S-3) were used to calculate the concentration of the iodine solution. This was compared with the known concentration and that from the bulk titration method. An average of three titration values is reported with the standard deviation.

#### 2.2.4 Statistical analysis

For quantitative analysis, differences between the known concentration of an acid and concentrations obtained from the bulk titration and the marble methods were analyzed using one-way ANOVA at 95% confidence level in Minitab 19.

# 3 Results and discussion

## 3.1 Qualitative analysis

Aqueous NaOH or NH<sub>4</sub>OH solution were added in drops or in excess to test-tubes or marbles of CuSO<sub>4</sub>·5H<sub>2</sub>O, FeCl<sub>3</sub>·6H<sub>2</sub>O, ZnCl<sub>2</sub>, Pb(NO<sub>3</sub>)<sub>2</sub> and CaCl<sub>2</sub> solutions and observed for characteristic reactions that indicate the presence of Cu<sup>2+</sup>, Fe<sup>3+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup> and Ca<sup>2+</sup> ions, respectively (Table 2). Similarly, test-tubes or marbles of aqueous Na<sub>2</sub>SO<sub>4</sub> and CaCl<sub>2</sub> were reacted with various test reagents in drops and in excess (Table 3), and observed for characteristic reactions that indicate the presence of SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> ions, respectively. The liquid marbles were stabilized by either fumed silica particles or fluorinated sericite clay particles. Chemical reaction between the marble content and the test reagents was possible because of the porous nature of liquid marble shells [5, 32, 33]. The addition of a test reagent solution to a marble increases its volume as well as its surface area at a fixed particle coating. As a result, some regions of the marbles were uncoated by particles. Although this may potentially increase the evaporation of the marbles [34], the marbles did not crumble or buckle [35, 36] within the time frame of the experiment. Generally, the formation of a colored or colorless precipitate that is soluble or insoluble in excess of the test reagent solution is a common feature of many inorganic qualitative analyses. This is very easy to observe in transparent glass test-tubes. Suffice it to say that marbles will be suitable for such analyses if they are transparent enough to clearly observe precipitate formation. Transparent marbles have been prepared previously from fumed silica particles [37]. On this basis, relatively transparent marbles from silica particles and marbles from sericite clay particles were used. Marble formation and hence the reactions were possible with all the particles, 14–61% SiOH silica and PF-5 to 12 fluorinated sericite clay, under investigation. Test-tubes and marbles showing results of some qualitative analyses are shown in Fig. 3 and Figs. S-1 to S-5.

Unlike in the transparent glass test tubes where all the characteristic precipitates were clearly visible, only colored precipitates like those from  $CuSO_4$  and NaOH solutions were visible in the marbles. White precipitates like those formed between Pb(NO<sub>3</sub>)<sub>2</sub> and NaOH solutions were more visible in marbles formed by silica particles than those formed by the sericite particles.

## 3.2 Quantitative analysis

Acid solutions of known concentrations were standardized by titrating against bases of known concentrations in the presence of suitable indicators to the end-point using bulk titration and liquid marbles. Liquid marble titration was performed below the maximum critical volume (100  $\mu$ L) above which it collapses. Unlike with the bulk titration where it is difficult to determine the range at which color change occurs, that  $(\pm 5 \mu L)$  for the liquid marble method can be obtained from the difference in volume of the marbles. The concentration of an acid, calculated from its volume at the end-point from these methods was compared with its known concentration using one-way ANOVA at 95% confidence level. Results for the bulk titration and liquid marble (Fig. 4 and Figs. S-6 to S-13) methods are shown in Table 4 for equimolar (0.6 M) NaOH and HCl solutions and in Table 5 for 0.6 M NaOH and 0.2 M HCl solutions. Results for other acid-base systems and between iodine and  $Na_2S_2O_3$  solutions (redox titration) are shown in Tables



**Fig. 3** (Left) **a** Photographs of a test-tube containing 2 cm<sup>3</sup> CuSO<sub>4</sub> solution (1 M): **i** alone, **ii** plus drops, and **iii** excess of NaOH solution (0.6 M). **b–d** Photographs of CuSO<sub>4</sub> solution (1 M) liquid marbles (40  $\mu$ L): **i** alone, **ii** plus 10  $\mu$ L NaOH solution (0.6 M), and **iii** plus 25  $\mu$ L NaOH solution (0.6 M). (right) **a** Photographs of a test-tube containing 2 cm<sup>3</sup> Pb(NO<sub>3</sub>)<sub>2</sub> solution (1 M): **i** alone, **ii** plus drops, and **iii** excess of NaOH solution (0.6 M). **b–d** Photographs of Pb(NO<sub>3</sub>)<sub>2</sub>

solution (1 M) liquid marbles (40  $\mu$ L): **i** alone, **ii** plus 10  $\mu$ L NaOH solution (0.6 M), and **iii** plus 25  $\mu$ L NaOH solution (0.6 M). The arrows indicate regions of precipitate formation. This is clearly visible in CuSO<sub>4</sub> solution liquid marbles which form colored precipitates as opposed to in Pb(NO<sub>3</sub>)<sub>2</sub> which form white precipitates. The marbles were stabilized by: **b** Aerosil R202 silica particles, **c** 61% SiOH silica particles and **d** PF-12 fluorinated sericite clay particles



S-4 to S-10. Each result is an average of three separate titrations and is reported along with the standard deviation. We envisaged two sources of errors with the liquid marble method, namely 'evaporative error' where the drop loses water [35, 36] and becomes more concentrated and 'competitive error' where the OH part of the SiOH group on silica particles produces H<sup>+</sup> ions that compete for OH<sup>-</sup> ions with the H<sup>+</sup> ions of the acid [30]. A concentrated drop will require more hydrogen ions, altering the end-point. Also, the end-point and hence the concentration of acid calculated will depend on the amount of H<sup>+</sup> ions released by a given silica particle type (characterized by %SiOH). We hypothesized that the higher the %SiOH, the higher the amount of H<sup>+</sup> it releases in line with [30, 31]. On this basis, silica particles of varying %SiOH were used and compared

with the fluorinated sericite particles, which do not have  $H^+$  ion releasing potential, so as to investigate this effect. It turns out that the end-point and concentrations of acid calculated are unaffected by %SiOH. The concentration values compare favorably ( $p \le 0.05$ ) with those from the bulk titration method as well as the known concentrations of the acids irrespective of the silica or sericite particle type. This means the amount of  $H^+$  ion released from the silica particles and evaporation (within the experimental timeframe) have no effect on the result and that the marble method is as reliable as the bulk titration method. Using the liquid marble method offers numerous advantages in comparison to the bulk titration method. The marble method generates little waste as microliter volumes of solutions are required. Because microliter volumes of

**Table 4** Calculated concentrations of HCl solution from its volume at the end-point for titration against NaOH solution (0.6 M), where the known concentration of HCl solution is 0.6 M, from the bulk and liquid marble titration methods. The marbles are stabilized by silica or fluorinated sericite clay particles

	Calculated (HCI)/M
Bulk	$0.60 \pm 0.00$
Aerosil R202 marbles	$0.66 \pm 0.06$
Silica (61% SiOH) marbles	$0.60 \pm 0.00$
Silica (50% SiOH) marbles	$0.60 \pm 0.00$
Silica (33% SiOH) marbles	$0.60 \pm 0.00$
Silica (14% SiOH) marbles	$0.60 \pm 0.00$
PF-5 Fluorinated sericite marbles	$0.60 \pm 0.00$
PF-8 Fluorinated sericite marbles	$0.60 \pm 0.00$
PF-12 Fluorinated sericite marbles	$0.60 \pm 0.00$

**Table 5** Calculated concentrations of HCl solution from its volume at the end-point for titration against NaOH solution (0.6 M), where the known concentration of HCl solution is 0.2 M, from the bulk and marble titration methods. The marbles are stabilized by silica or fluorinated sericite clay particles

	Calculated (HCl)/M
Bulk	$0.24 \pm 0.01$
Aerosil R202 marbles	$0.22 \pm 0.02$
Silica (61% SiOH) marbles	$0.22 \pm 0.02$
Silica (50% SiOH) marbles	$0.22 \pm 0.02$
Silica (33% SiOH) marbles	$0.22 \pm 0.02$
Silica (14% SiOH) marbles	$0.22 \pm 0.02$
PF-5 Fluorinated sericite marbles	$0.22 \pm 0.02$
PF-8 Fluorinated sericite marbles	$0.22 \pm 0.02$
PF-12 Fluorinated sericite marbles	$0.22 \pm 0.02$

solutions are used, little amount of reagents are used per experiment thus saving cost. Above all, the liquid marble method can easily be integrated into a digital device and applied in microfluidics [20].

# 4 Conclusions

The use of liquid marbles as microreactors for qualitative identification of inorganic cations and anions and quantitative acid–base and redox titrations have been demonstrated by simply placing a test reagent solution on a marble, where it merges and initiates a chemical reaction. This is in contrast to previous experiments which require the use of a force field to initiate the coalescence of liquid marbles [19, 20]. This was possible due to the porous shell of liquid marbles [5, 32, 33]. For qualitative analysis, colored precipitates like those formed between CuSO<sub>4</sub> and NaOH

solutions were easily visible in the liquid marbles of both the silica and sericite particles while white precipitates like those from Pb(NO<sub>3</sub>)<sub>2</sub> and NaOH solutions were easily visible in marbles formed by silica particles compared to those formed by the sericite particles. The effect of %SiOH of silica on the end-point was studied and compared with the fluorinated sericite clay particles without H<sup>+</sup> ion releasing potential for the quantitative analysis, but the endpoint was unaffected by %SiOH. Unlike previous reports [19, 20] on acid-base reactions in liquid marbles without information on end-point and reliability of the method, we show that the concentration of acid, calculated from the volume at end-point, agrees closely ( $p \le 0.05$ ) with that from the conventional bulk titration method. This indicates the reliability of the marble method. Because microliter volumes of solutions and by extension the chemicals utilized are small, the liquid marble approach has the advantage of producing relatively small amount of waste, compared to methods that require relatively large volumes of solutions. Although microfluidic lab-on-a-chip devices [28] utilize smaller volumes than those reported here with the liquid marble method, they are reaction-specific and require microchannels and external pumps to facilitate the manipulation of the liquids. Even when such devices are modified to work without microchannels [29], sample contamination is still a major concern; meaning that the liquid marble method is a plausible alternative to the bulk conventional method in microfluidics. Finally, the choice of particles (fumed silica and fluorinated sericite clay) used here is not restrictive; the work can be extended to other suitable particles.

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## **Compliance with ethical standards**

**Conflict of interest** The authors declare that they have no conflict of interest.

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