SUPER-RESOLUTION *IN SITU* ULTRASONIC MONITORING OF CHEMICAL REACTIONS

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Abstract - This paper describes experiments to compare the sensitivity and robustness of ultrasound measurements with pH measurements when monitoring chemical reactions under laboratory conditions, the aim being to determine the relative suitability of the two techniques for process monitoring and control. It is shown that ultrasonic time-of-flight measurements, based on the centre of area of an ultrasonic pulse provides for super-resolution with respect to the sampling frequency. In comparison to reaction monitoring based on pH measurements, ultrasound was found to be superior in terms of its response time and resolution.

I. INTRODUCTION

Ultrasonic measurements have been extensively used for studies of various aqueous solutions, and the results obtained have been related to the thermodynamic and/or chemical properties of the test media [1,2]. However, due to the technological limitations to early ultrasound techniques the methods were only of limited applicability even under laboratory conditions. Recent improvements in the accuracy and versatility of ultrasonic instruments allows for reliable measurements to be performed within milliseconds [3], and tracking chemical and physical transformations in real time [4].

A number of industrial processes involve phase transformations of inorganic chemicals, such as coagulation-precipitation of metal ions as hydroxides. Examples of large-scale applications include domestic waste water treatment using aluminium and iron salts; preparation of industrially important materials such as metal hydroxides and oxides using sol-gel or other processes involving colloid formation and/or precipitation in metal ion solutions. Since the process of metal ion transformation into colloidal and solid states is generally pH-dependent, pH measurements are the most frequently used methods for monitoring the reactions occurring in metal ion aqueous solutions during these transformations e.g. by alkaline neutralisation. One of the most common approaches involves acid-base titrations, where metal ions serve as an acid and they are neutralised by the addition of various bases.

The purpose of this study was to compare the sensitivity and robustness of ultrasound to pH measurements when performed ***in situ*** under conditions used by a chemical practitioner with a view to assessing their appropriateness for monitoring and ultimately control of processes involving metal ion solutions.

II. CHEMICAL BACKGROUND, INSTRUMENTATION AND PROCEDURES

Two model chemical systems were used in which pH was varied either by addition of metal ion solution to an acidic solution, or an acid-base titration of an aqueous solution of aluminum chloride with potassium hydroxide at high concentrations of both. The first system ($AlCl_3$ + HCl) was chosen with a view to measuring the increasing concentration of Al ions in a titration-like fashion, without hydrolysis of the Al ions. The second model system, Al ion solution neutralized with KOH, was chosen to bring about very fast changes caused by the addition of small drops of strong concentrated alkali (KOH) to aluminum ion solutions of medium concentration.

Experiments on the variation of aluminum chloride concentration in hydrochloric acid solution (Experiment 1, ‘Exp 1’) and on acid-base titration of aluminum chloride solution with potassium hydroxide (Experiment 2, ‘Exp 2’) were conducted using the experimental set-up shown in Fig. 1. The

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solutions and titrants used are described in the table. Four distinct chemical processes can occur during the acid-base titration of Al ions; the details of these processes can be found in [9].

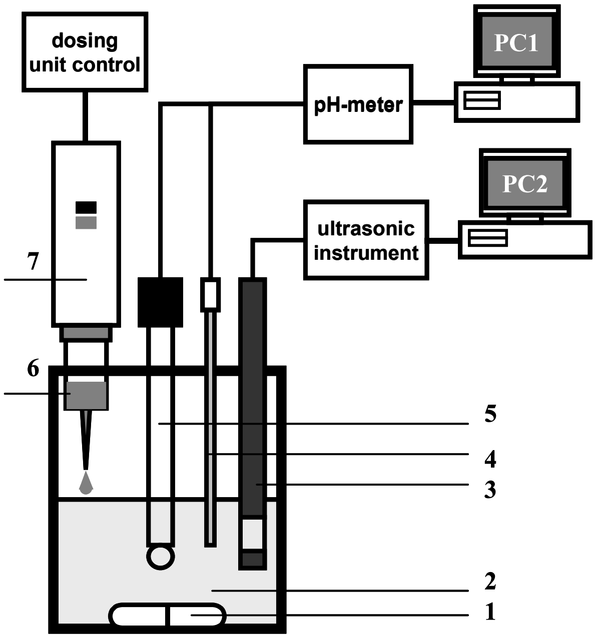

Fig.1. Schematic of the experimental set-up (1 – magnetic stirrer, 2 – test solution, 3 – ultrasonic probe, 4 – temperature probe, 5 – pH probe, 6 – tip of the dosing unit, 7 – dosing unit)

	Solution	**Titrant**
Exp 1	HCl 0.943 mol/L 100 mL (A)	$AlCl_3$ 0.635 mol/L 0.4 mL/drop
Exp 2	$AlCl_3$ 0.156 mol/L 100 mL (B)	KOH 2.863 mol/L 0.2 mL/drop
pH≤3.0	*(1)* $\mathbf{Al(H_2O)_6^{3+} \rightarrow Al(OH)_y(H_2O)_{6-y}^{3-y} + yH_3O^+}$	
pH≥3.5	*(2)* $\mathbf{xAl^{3+} + yOH^- \rightarrow Al_x(OH)_y^{(3x-y)+}}$	
pH~6-7	*(3)* $\mathbf{AlCl_3 + 3KOH \rightarrow Al(OH)_3\downarrow + 3KCl}$	
pH>8	*(4)* $\mathbf{Al(OH)_3\downarrow + OH- \rightarrow Al(OH)_4^-}$	

A glass chemical beaker (125 ml) was used as a titration vessel and was mounted on the surface of a magnetic stirrer. The sample solutions were degassed for 15 min in an ultrasonic bath and then added to the titration vessel. A magnetic stirrer bar and three probes were immersed into the sample solution in the vessel: The *Red Rod* combined a glass pH-electrode (Radiometer) with a thermo-sensitive glass-coated probe, both connected to a pH-meter (PHM240, Radiometer); the third probe was an ultrasonic sensor, described below.

After initiation of stirring at a constant speed of 350 rpm and equilibration of the titration cell for 10 min, additions of titrant solution were made at equal time intervals (30 sec – Exp 1; 60 sec – Exp 2). Readings of pH and temperature were taken every 2 sec and recorded on a PC interfaced to the pH-meter. Titrant addition was carried out using an EDOS 5222 automatic liquid handling unit (Eppendorf) as an autotitrator. The plastic piston tips (Combitips, Eppendorf) of the dosing unit were changed between the experiments. The theoretical resolution of the pH probe was 0.002 units of pH and its temperature resolution was 0.1 °C; the imprecision of EDOS autotitrator was <2% at the minimum dose of 0.2 ml.

III. ULTRASONIC INSTRUMENTATION AND SIGNAL PROCESSING

An arbitrary function generator (AFG) instrument [5] was used to excite an ultrasonic transducer (V-317, 20 MHz, Panametrics Inc.) in the pulse-echo mode, amplify the echo received, and digitise and store the relevant part of the waveform. It was set to an automatic recording mode acquiring a waveform each 2 seconds without averaging. The transducer was housed in a stainless steel custom-made tube opposite to a stainless steel reflector. Provision was made for adjusting the ultrasonic gauge length before an experiment.

The acquired data were processed offline using MATLAB. A range of ultrasonic propagation variables was investigated in relation to their suitability for robust and reliable monitoring of the solution. Most of them were rendered significantly variant by electronic noise [6] and also by bubbles and other inhomogeneities in the reaction vessel. It was found that estimates of time-of-flight or group velocity based on the integral properties of the received pulse [7] gave the most robust track of the chemical reaction provided that data transmission and sampling equipments were adequately synchronised to minimise timing jitter [8].

The received ultrasonic data was processed in three steps: Rejection of corrupted records, setting the data capture window, and calculating the centre of area (CoA) of the received pulse as a timing marker.

IV. MONITORING THE CONCENTRATION (EXPERIMENT 1)

The concentration of the titrant, aluminum ions, introduced as $AlCl_3$ solution, was varied monotonically from $5*10^{-4}$ mol/L after the first addition of the titrant to ca. 0.3 mol/L at the end of experiment. A high initial concentration of hydrochloric acid (0.943 mol/L) served to prevent hydrolysis of aluminum ions. The volume of titrant added was proportional to the time into the titration. The weight change in chemical composition after a titrant drop was less than (because the denominator – the mass of the solution in the beaker - increased over time):

$$\frac{(0.4\times10^{-3}L)\times(0.635mol/L)\times(133.33g/mol)}{100g}=$$

$$0.000339\approx0.03\%=300ppm$$

Fig. 2 shows part of the experimental pH and ultrasound responses. The ultrasonic method had a faster response time with greater resolution, implying its suitability for process monitoring

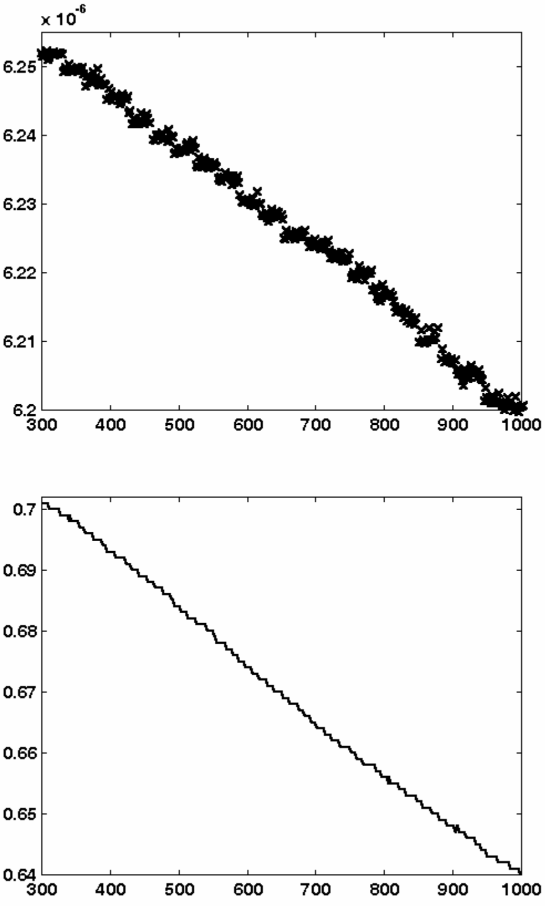

Fig.2. Top: Ultrasonic centre-of-area (s), and (bottom) pH estimates versus time (s) for exp. 1.

V. MONITORING AN ACID-BASE TITRATION (EXPERIMENT 2)

This experiment involved acid-base titration of medium concentration aluminum chloride solution with highly concentrated strong alkali – potassium chloride. The weight change in chemical composition after a titrant drop was less than

$$\frac{(0.2\times10^{-3}L)\times(2.8628mol/L)\times(56.1g/mol)}{100g}=$$

$$0.000321\approx0.03\%=300ppm$$

The results on fig.3 show that the ultrasound CoA signal falls in a similar fashion to the rise in the pH during the titration. This implies that ultrasound could provide a viable substitute for pH in process monitoring. Fig. 4 shows a zoom-in to

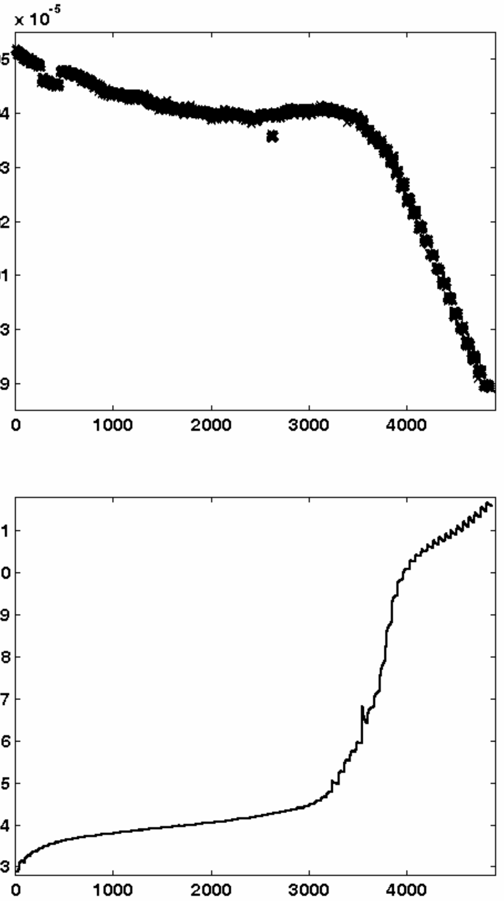

Fig.3. Top: Ultrasonic centre-of-area (s), and (bottom) pH estimates versus time (s) for exp. 2.

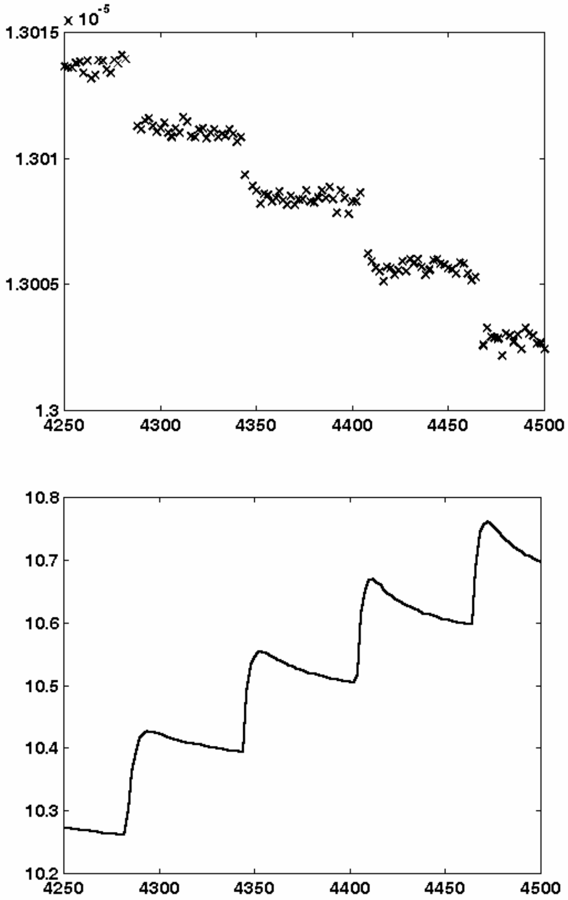

Fig.4. Top: Ultrasonic centre-of-area (s), and (bottom) pH: Zoomed estimates versus time (s) for exp. 2. The steps correspond to titration droplet addition.

part of the data of fig. 3. The pH shows a slow rise in response to titration droplet addition, with a settling time of around 25s. By comparison, the ultrasonic response clusters show a step-down in less than 2s at each droplet addition. Analysis of individual clusters in the ultrasonic trace indicates that the variation within each cluster was of the order of 1ns, much less than the digitizer resolution of 3.1ns.

Limitations of space have prevented us from presenting comprehensive details of the complex course of the chemical changes during titration, see [9], and indeed, the ability of ultrasound to track significant events in the process. However we have found ultrasound to be sensitive to three key phenomena – the monomeric hydrolysis of Al-ions; the collapse of Al tridecameric polycations $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$, and the bulk precipitation of aluminum hydroxide.

VI. CONCLUDING REMARKS

The results of the above experiments show that ultrasonic monitoring of titration reactions produces broadly equivalent data to that obtained through pH measurements. Ultrasound was superior to pH monitoring in terms of its resolution and response time – less than 2s compared to 25s. Further, ultrasonic probes can be made in robust form and applied to the exterior walls of process pipe-work whereas pH probes require to be immersed in the reacting fluid and are therefore prone to erosion damage.

Use of the pulse CoA to estimate time-of-flight or group velocity provided timing resolution which appeared exceed that of the digitizer, although the statistical certainty of this remains to be established. Further developments of ultrasound sensing systems will improve functionality - these include compensation for working temperature, self calibration, and the incorporation of tracking algorithms based on process models. Finally, miniaturization of the supporting electronic systems will reduce cost and will improve robustness and accessibility to process plant.

VII. REFERENCES

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