DISCONTINUOUS FLOW ANALYSIS : A UNIQUE APPROACH TO FLOW-BASED TITRATIONS.

T.J. Cardwell¹, R.W. Catrall¹, J.D. Petty², and G.R. Scollary³

Centre for Scientific Instrumentation, La Trobe University, 3083, Australia (1); Ionode Pty Ltd, PO Box 52, Holland Park, 4121, Australia (2); School of Science and Mathematics, University of Melbourne, 3052, Australia (3).

Abstract The operating principles of the new flow-based technology, Discontinuous Flow Analysis, are described. The uniqueness of this technique for flow titrations is discussed and examples of titrations using potentiometric and indicator detections are given. The suitability of Discontinuous Flow Analysis for process control is discussed.

Keywords Discontinuous flow analysis, flow titrations, process control.

The new flow-based instrumental technology, entitled Discontinuous Flow Analysis (DFA), has been developed by Petty *et al* and patented to Ionode Pty Ltd (Brisbane, Australia) [1]. In the simplest form of this flow technique, two pumps are used : one discharge and one suction, the discharge pump being connected to a reagent reservoir. These pumps are placed either side of the sample inlet and are driven by interchangeable cams (See Fig 1). During the measurement half-cycle, determined by the cam section X, suction pump P2 operates at constant velocity whilst the velocity of discharge pump P1 is varied. Depending on the relative flow rates of P1 and P2, it is possible at various times during the flow cycle for sample only, reagent only or a combination of the two to be conveyed to a detector. At the completion of the measurement half-cycle, valves V1 and V2 switch and the refill half-cycle (cam section Y) commences. Pump P1 refills with reagent from the reservoir (R), whilst P2 expels to waste. An encoder is attached to the driveshaft of the cam which allows the output of the detector to be recorded as a function of the cam position [2].

The significant conceptual difference between this new development and existing flow based methods is the ability to vary the flow rates of one or more pumps in a highly reproducible manner. Depending on the cam profile, the flow rates of the pumps can be programmed so that a wide variety of flow analysis methods becomes accessible. This allows automated flow titrations to be readily performed.

Fig 1. Schematic layout for the DFA pump and cam arrangement.

Fig 2. Flow cell design used in DFA showing the vibrating reed mixer.

Flow Titrations with Potentiometric Detection

Titration of calcium with EGTA using a calcium ISE as sensor and acid/base titrations using glass and PVC membrane-based pH sensors have been described [2,3]. A schematic flow cell is shown in Fig 2. Mixing of the sample and reagent components is achieved using an efficient vibrating reed mixer [4]. A typical DFA trace for the

determination of the acidity of a vinegar sample is given in Fig 3. At point A, sample (vinegar) is aspirated into the flow cell, the sensor rising to a maximum at B. Titrant (base) is added rapidly to establish a flow rate ratio of 2 : 1 (sample to titrant). The flow rate ratio is then varied continuously until, at point D, the flow rate ratio is 1 : 2 (sample to titrant). The endpoint in the titration (C) occurs at some critical flow rate ratio between these two extremes and can be easily identified from the derivative plot, readily obtainable from the software used to monitor the process [3].

Titration of this type have been successfully applied to the determination of calcium in waters and wines [2] and to the determination of the total acidity of vinegars and the titratable acidity of wines [3].

Fig 3. DFA titration curve for the determination of the acidity of a vinegar sample.

Flow Titrations with Indicator Detection

The procedure followed is similar to that described above for titrations with potentiometric detection except that a third pump must be included to allow the addition of the indicator [2]. This third pump is placed on the suction side of the cam, except that its operation is reversed to that of P2 in Fig 1, so that indicator is discharged at a constant rate during the measurement half-cycle. Detection is achieved with a light emitting diode (LED) in combination with a photodiode, the choice of LED being dependent on the indicator selected [4]. A highly efficient turbine mixer has also been developed as part of the flow cell for this type of flow titration [4]. Acid/base [4] and EDTA complexation [5] titrations can be performed using indicator detection.

It is also possible to use the quinone/hydroquinone redox couple as an indicator for acid/base titrations. The potential of this couple depends only on pH, and using a flow cell containing two platinum electrodes, it is possible to monitor differential changes in pH during the flow titration. This method of detection is most successful for samples which show a sharp change in pH at the endpoint [3].

Industrial Applications

Various industrial applications of DFA have been examined, the overall intention being to develop instrumentation suitable for process control.

The sulfuric acid content of the absorber liquor used to recover ammonia from raw Coke Ovens gas in a steel mill has been determined by DFA flow titration [6]. Indicator/spectrophotometric detection is used for endpoint determination. The DFA procedure compares favourably with manual and autotitrator methods and relative standard deviations are between 2 and 3%. A significant advantage of the DFA procedure is that the calibration remained constant over a four week test period, recalibration only being required when the reagents were changed [6].

A procedure has been developed for the determination of the alumina content and the caustic soda content of Bayer liquor using thermometric detection [7,8]. Sodium potassium tartrate and potassium bicarbonate are used as titrants for the alumina and caustic soda respectively. The unique features of this DFA process include on-line dilution of the sample, on-line cooling of the flow cell and a single cam capable of titrating two sample analytes.

Indicator/spectrophotometric detection has been found to be suitable for the analysis of zinc and sulfuric acid in zinc plant electrolyte [5]. Zinc is measured by titration with EDTA using alizarin complexone as indicator and the sulfuric acid content is determined using sodium hydroxide as titrant with bromocresol green as indicator. The DFA flow titrations agree favourably with standard industry procedures.

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