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A monosegmented-flow Karl Fischer titrator

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Abstract

A monosegmented volumetric Karl Fischer titrator is described to mechanize the determination of water content in organic solvents. The system is based on the flow-batch characteristics of the monosegmented analysis concept and employs biamperometry to monitor the progress of the titration. The system shows accuracy and precision that are highly independent of the flow rate, does not require calibration, and is carried out in a closed system capable of minimizing contact of the sample and reagents with ambient moisture. Sample volumes in the range of 40–300 μL are employed, depending on the water concentration. An automatic dilution is provided to deal with concentrated samples. The consumption of Karl Fischer reagent depends on the water content of the sample but is not larger than 100 μL. The system was evaluated for determination of water in ethanol and methanol in the range 0.02–0.5% (w/w). The average relative precision estimated in that range (9–3%) is comparable to that obtained with a larger volume commercial system and no significant difference was observed between the results obtained for the two systems at the 95% confidence level. A complete titration can be performed in less than 5 min employing the proposed system.

Keywords: Water determination; Mechanized titration; Monosegmented analysis; Karl Fischer titration; Flow-batch analysis; Ethanol; Methanol

1. Introduction

The determination of water in several types of sample matrices using the Karl Fischer titration is one of the highest demand determinations of a single analyte determination. The number of daily determinations has been estimated to be above 500,000, in samples as diverse as food, isolating oil, pharmaceuticals, hydrocarbons and pure organic solvents such as alcohols [1].

There are many papers describing the mechanization of the Karl Fischer method with resulting improvements in sample throughput and reduction of sample and reagent consumption. Also, mechanization can provide analytical systems capable of manipulating hazardous substances employed in the composition of the Karl Fischer reagents, avoiding exposition of the operator and minimizing laboratory residues. Although the toxicity of this reagent has been reduced over the years [2] its composition and the residues it produces still require attention.

The Karl Fischer method has been automated by using the flow injection (FI) principle [3–9]. The main advantage of the FI-based method is sample throughput and the possibility of kinetic discrimination of interfering side-reactions. The greatest disadvantages of those systems are the need of analyte standards to calibrate the system and its critical dependence on flow rates.

Flow-batch systems have recently been proposed [10–12] based on multicommutation and the use of open chambers where titrations can be processed. They present an interesting option to automate the Karl Fischer titration, although they have not yet been described for this purpose. On the other hand, the system requires the use of a mixing chamber and the volume of sample, reagents and diluents are heavily dependent on the flow rate determined by the impelling devices, such as peristaltic pumps, affecting precision.

The monosegmented flow analysis concept [13] has been also applied to automate titration-based analytical methods [14–18]. However, the full exploitation of the concept as a flow-batch system, and its use to perform Karl Fischer titrations has not yet been described. The liquid monosegment, limited by the axial front and back air borders inside a tube, can be in fact visualized as a sample aliquot present in a vessel. The first titrator proposed, based on the monosegmented flow concept [17], employed the movement of the monosegment for a long distance inside a small bore tube in order to achieve homogenization after titrant addition, before spectrophotometric determination of the mixture.

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This long tube approach forbids the use of electrochemical techniques, such as biamperometry and potentiomety, to monitor the progress of the titration because the monosegment has to be moved away from the detection cell. For a spectrochemical-based detection this operation is possible without causing serious trouble to measurement precision. However, for an electrochemical cell, the system becomes unstable due the alternating contact of air and liquid (titrated solution) with the electrodes.

This work describes a monosegmented flow-batch titrator system employing biamperometry to monitor the progress of Karl Fischer titrations. The system performs true titrations and precludes any calibration. The volume of the injected monosegment, the concentration of the Karl Fischer reagent and the volume required to achieve the end point of the titration are the only parameters necessary to perform the analysis. The system differs from those previously described [17,18] because part of the monosegment is always in contact with the detection cell and the homogenization is carried out by cycling between two points around the cell. This also contributes to a significant reduction in the size of the titrator.

The system has been evaluated for the determination of water in ethanol and methanol. The importance of determination of water in these two substances, and principally in the first, becomes evident if one considers that in Brazil, as in several other countries, the gasoline sold in fuel stations contains about 25% added absolute ethanol.

2. Experimental

2.1. Reagents and solutions

Analytical grade reagents and solvents and deionised water were employed throughout. Synthetic samples of methanol containing different amounts of water in the range 0.01–0.5% were prepared by addition of water to methanol previously dried for 24 h over activated molecular sieves (4A, Carlo Erba). Dried methanol was also used as diluent for highly concentrated samples. The water content of this dried methanol was estimated to be about 0.008% (w/w) by conventional Karl Fischer titration. When the dilution procedure was employed, a blank was run to account for the water content in the diluting solvent.

The Karl Fischer titrant solution was a commercial Combititrant 5 (Aquastar). A 1 μL of this solution reacts with 5.0 μg of water. The strength of this solution was checked by titrating methanol samples prepared to contain known amount of added water.

2.2. Equipment

The results of the titrations made with the proposed system were compared with those obtained by using a commercial batch titrator (Orion AF8). That system employs the biamperometric technique to locate the end point.

2.3. Monosegmented titrator

Fig. 1a shows a diagram of the proposed Karl Fischer monosegmented titrator, which is similar to the previously described titrators [17,18]. However, the titration procedure itself has been substantially altered. The syringe/step motor-based system employed for volumetric additions of the Karl Fischer reagent uses a gas-tight syringe of nominal volume equal to 500 μL and can deliver volumes with a precision of ±0.5 μL. A peristaltic pump (Ismatec IP8) was employed to impel the fluids in the system. The pump is controlled by the system microcomputer through a standard serial interface (RS-232). Besides controlling the peristaltic and syringe pumps, the microcomputer also controls three miniature three-way electromechanical valves (National Research, NR 161T031-12VDC) used to admit the washing solution (V_1), to allow for titrant refill of the syringe pump (V_2), and to avoid moisture entering the system through the waste tubing during the cycling operation of the monosegment (V_3). The microcomputer also monitors the logical state of three optical switches (PHCT 203) employed to locate the monosegment during the homogenization cycles. All these operations are made through a parallel interface (PCL 711S, Advantech) which contains a 12 bit analog-to-digital converter to allow for current measurement of the biamperometric detector, 16 digital outputs for valve control and 16 digital inputs for to access the logical state of opto-switches. The circuit for the detector is depicted in Fig. 1b. The potential difference applied to the electrodes was 250 mV.

The system has some points through which external moisture could enter, possibly altering the results of a titration. This is a constant source of concern even for automated batch systems. In the present system, moisture could find access through the air stream employed to carry the monosegment, through the washing solvent reservoir, through the titrant reservoir and through the air input from the tubing after the cell, when the cycling operation is moving the monosegment forward and backward. All these points have been protected against access of external moisture by using molecular sieve traps and by keeping (when possible) the solvents over molecular sieves.

Fig. 2a shows a detail of the sample introduction port. The device is made of Teflon® to allow working with organic solvents. The arrangement of the three loops, as shown, has been previously reported for the purpose of diluting a sample segment [19]. It is possible to note that, when the sample is injected using the device herein described, the contents of the three loops are simultaneously inserted into the system, carried by a dried gas stream while the central segment, containing the sample, is merged with the other two segments containing a diluent. The mixture is then passed to the next stage of the titrator.

Fig. 3 shows the flow-detection cell employed for biamperometric monitoring of the Karl Fischer titration. The cell was made of a 2 cm × 3 cm × 1 cm Teflon® block. The platinum electrodes were made of two metallic rods with 2 mm diameter, inserted perpendicularly to the cell body. Two optical-switches were placed 1 cm before and 1 cm after the flow cell to detect the location of the monosegment.

2.4. Titration processing

The titration of a sample starts when the user moves the injection port to the direction indicated in Fig. 2a (left). The

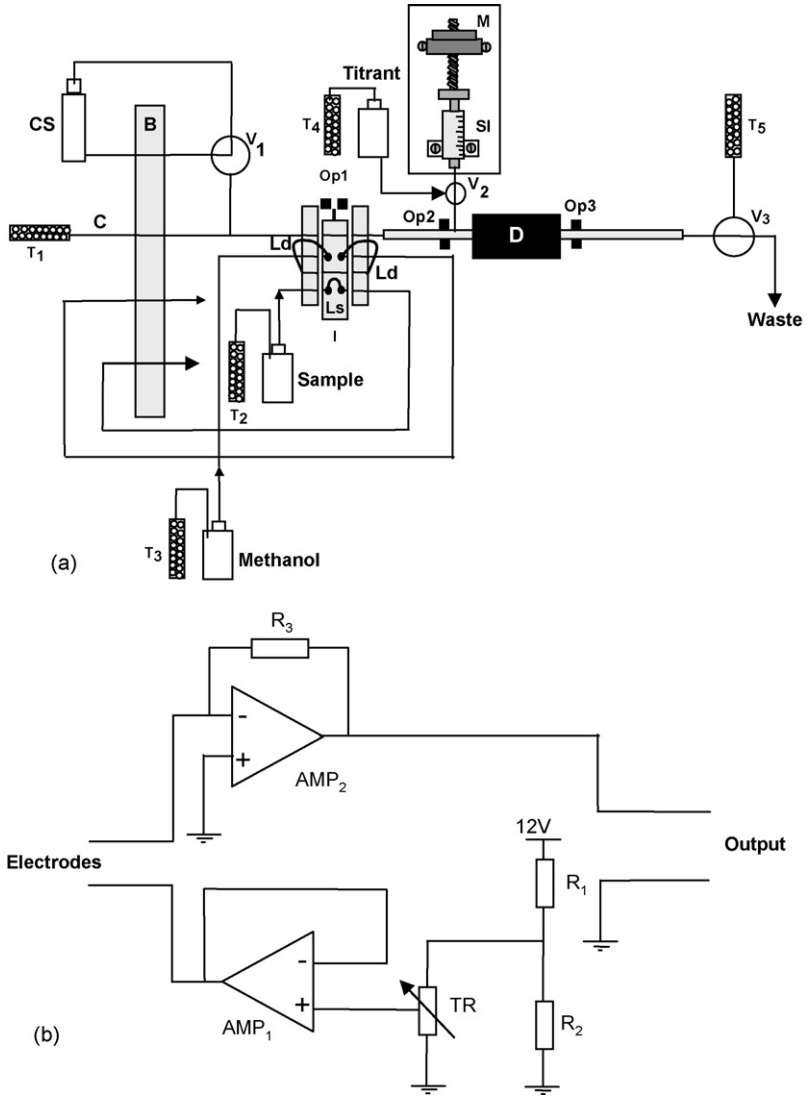

Fig. 1. (a) Schematic diagram of the Karl Fischer monosegmented titrator. CS, washing fluid (methanol dried over activated molecular sieve); C, dry air or dry nitrogen carrier gas; Ld, diluent loops; Ls, sample loop; I, injection port; $Op_{1–3}$, optical switches; D, biamperometric cell; $V_{1–3}$, three way electromechanical valves; SI, gas-tight syringe; M, stepper motor, $T_{1–5}$, traps containing activated molecular sieve. (b) Biamperometric detection circuit. TR, 10 kΩ trimpot; R_1, R_2 and R_3, resistors 10 kΩ, 2.2 kΩ and 1 MΩ, respectively; AMP_1 and AMP_2, 741 and 356 operational amplifiers, respectively.

sample introduction is detected by the microcomputer through OP1. The solutions contained in the three loops are simultaneously transported by an air carry stream to the titration cell. The segment formed by merging the loops volumes is stopped when its left air/liquid interface reaches the first opto-switch (OP_2). If a low concentration of water is present in the sample, all three loops are filled with the sample avoiding its dilution. If this is not the case, the monosegment is homogenized by cycling the monosegment position between the optical-switches surrounding the detection cell. The number of cycles is determined by the user. After homogenization (if necessary) the segment is stopped again with its right air/liquid interface at optical-switch (Op_3) also placed on the right side of the cell. The syringe pump delivers a pre-determined volume of titrant controlled by the number of steps sent to the motor. Typical volume increments vary from 5 to 20 μL. After titrant addition, the monosegment is again cycled to promote the reaction between titrant/titrand and the homogenization of the titrated mixture. Of course, the cycling operation, besides promoting the contact between the analyte and reagent, also gives the time for reaction to proceed to the equilibrium. The overall effect of the physical mixing and reaction kinetics (mainly near the titration end point, where lower excess of reagents are present) need to be considered when selecting the ideal number of cycles to be employed. The term "homogenization" refers, in this work, to the achievement of a stable measurement of the biamperometric current after both the physical mixing and chemical reaction have been processed. Each homogenization cycle requires about 3 s to be processed at the flow rate employed for the carrier air stream (5.0 mL min^{-1}). This time increases as the volume of the monosegment increases after each titrant addition. The titration proceeds until the programmed number of titrant increments has been attained. Alternatively, a pre-set value of current, measured by the biamperometric detector, can be employed as a fixed ref-

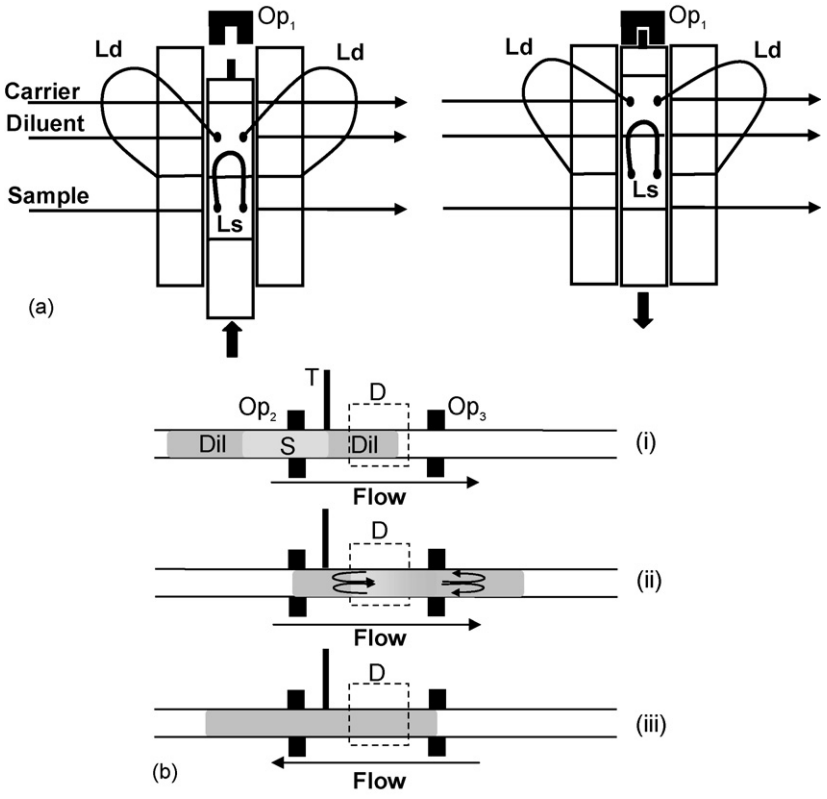

Fig. 2. (a) Arrangement of the reagent and sample loops in the monosegmented injection port (see Fig. 1 for other identifications); left, device in sampling mode; right, device in injection mode; Op_1, optical switch for identification of injector position. (b) Cycling operation for monosegment homogeneization. T, point of titrant addition; S, sample; Dil, diluent; D, biamperometric detection cell; Op_{2-3}, optical switches; i, ii and iii depict the three steps of one homogenization cycle.

erence value to stop titrant addition. A correction of the current value need to be performed before comparison with the pre-set value due the volumetric dilution caused by titrant addition. The corrected value is found multiplying the read value after each titrant addition by the ratio between the total volume of the segment (sample volume plus added titrant volume) and the initial sample volume. This is easily computed by the controlling software. The system is robust and does not show dependence of the flow rate established by the peristaltic pump. After finishing a titration, the system is washed by a segmented flow generated by turning the valve V_1 on for 10 s and pumping dried methanol to the confluence point with the gas carrier stream. Valve V_1 is then turned off and the methanol present in the system is flushed out by the air stream.

The resulting titration curves are stored and the end points are determined by the intercept obtained by extrapolating the two linear segments found before and after the titration end point.

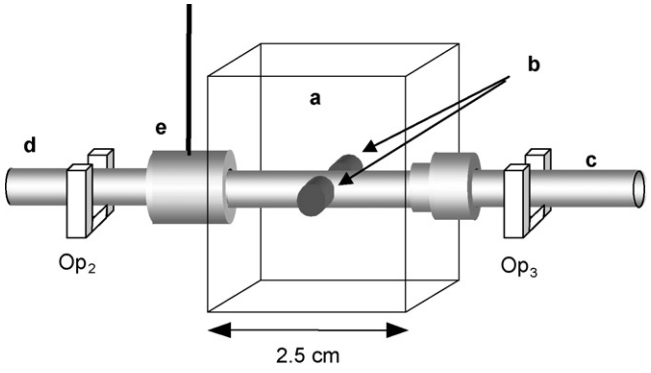

Fig. 3. Detection cell. (a) Teflon® block; (b) platinum electrodes for biamperometric detection; (d and c) Teflon® tubes; (e) point of titrant addition.

3. Results and discussion

The titration curve and, of course, end point location are affected by the number of cycles employed for monosegment homogenization. Fig. 4a shows the effect of the number of homogenization cycles on the biamperometric titration of a standard ethanol sample containing 0.76% (w/w) of water (sample loop = 40 μL, diluent loops = 2 × 85 μL, total monosegment volume = 210 μL). The effect of poor mixing and incompleteness of the reaction, mainly near the end point where the concentration of reagents (water and iodine) are lower, when using a number of cycles lower than 6 on the titration error is shown in Fig. 4b. The number of cycles necessary to achieve a homogeneous mixture of the titrated solution depends on the volume of the monosegment. This volume increases with the additions of titrant. Therefore, the number of cycles needs to be selected based on the prediction of the largest monosegment volume that will be produced up to the end of the titration. For an initial volume of 210 μL and titrant increments of 20 μL, necessary to titrate a sample containing up to 0.80% of water, eight homogenization cycles were required. This number drops to five cycles

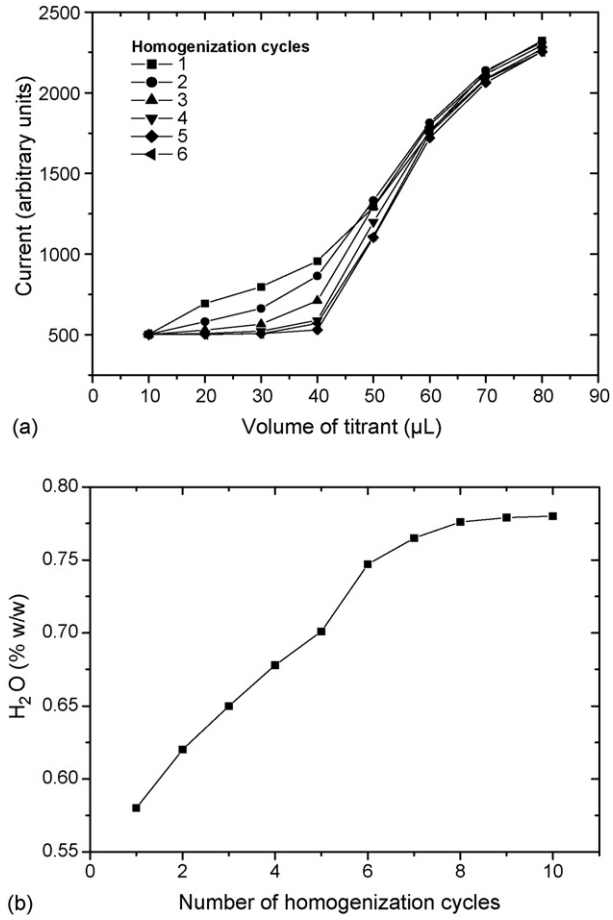

Fig. 4. Effect of the number of homogenization cycles after each titrant addition on the accuracy of the titration results. (a) Biamperometric titration curves of a 210 μL monosegment containing 0.76% (w/w) of water obtained with increasing numbers of homogenization cycles. (b) Effect of the number of homogenization cycles on the water concentration determined using the proposed system and the titration curves shown above.

for 5 μL increments when the titration involves water contents less than about 0.1%. The present system limits the minimum initial volume and the maximum final monosegment volume to 200 and 600 μL, respectively. The minimum volume is determined by twice the volume of the flow cell and the tubing path between the cell and the two optical-switches. The maximum volume is limited by the long time (excessive number of cycles) necessary to homogenize the monosegment composition and because larger monosegments are more prone to be disrupted during the cycling operation.

An upper limit of titratable water concentration can be increased by decreasing the volume of the sample loop (Ls) and diluting the sample using the two side loops (Ld) filled with a suitable diluent. By injecting 30 μL of sample and diluting it with two side loops of 135 μL to a final 300 μL volume, concentrations as high as 3% water can be titrated with the Karl Fischer solution employed in this work. If a higher concentrated titrant is available, higher water concentrations can be determined. Determinations at the lower concentration limit require that all three loops are filled with the sample to a total volume of 300 μL. The titrant syringe pump can deliver a minimum volume of 1 μL. Therefore, supposing that at least two points are necessary to define the linear segment before the end point in the biamperometric curve, the minimum titratable concentration, using the present Karl Fischer reagent solution, may be estimated as close to 0.005% (w/w).

Table 1 shows the results obtained for five replicate determinations of water in ethanol and methanol samples by the proposed titrator and by a commercial conventional batch titrator, employing the same Karl Fischer reagent. The results show a slightly better precision, expressed as the mean relative standard deviation, for the conventional (3.9%) system when compared with the proposed method (5.4%). The mean relative difference between the results is 5.4% with a predominance of somewhat lower results for the proposed titrator, that can be attributed to the higher risk of contamination of samples by external moisture in the conventional system, mainly for those samples presenting low water concentrations. Statistical analyses of the results showed that there are no significant differences between the results obtained by the two methods at the 95% confidence level.

Titrations, such as those shown in Table 1, can be performed in 3–5 min, depending on the number of titrant additions necessary. Of course, for routine determinations when concentration range of the sample can be anticipated, further optimization can reduce the titration time to the order of 2.5 min.

The presence of oxygen in the dried air carrier does not cause any significant effect on the determination of the end point of the Karl Fischer titrations. This was verified by using dried ambient air or dried nitrogen to carry the monosegment during the titration. Probably, it results from the small area of contact between the monosegment and the gas carrier stream.

Table 1
Results for determination of water in commercial samples of ethanol and methanol

Sample	Water content (%, w/w), proposed titrator (A)	Water content (%, w/w), conventional titrator (B)	Relative difference $[(A-B)\times 100/B]$ (%)
Ethanol 1	0.377 ± 0.014	0.409 ± 0.020	−7.8
Ethanol 2	0.514 ± 0.014	0.499 ± 0.017	3.0
Ethanol 3	0.538 ± 0.015	0.535 ± 0.008	0.6
Ethanol 4	0.268 ± 0.012	0.290 ± 0.006	−7.6
Methanol 1	0.0298 ± 0.0028	0.0329 ± 0.0021	−9.0
Methanol 2	0.0453 ± 0.0042	0.0473 ± 0.0025	−4.2

For ethanol: sample volume = 40 μL, volume of the monosegment after dilution = 270 μL. For methanol: sample volume = 270 μL (without dilution). The standard deviations refer to five determinations for each method and each sample.

The consumption of sample and reagents in the proposed system can be considered as its principal advantage over other automated Karl Fischer titrators. The average consumption of Karl Fischer reagent is typically lower than 100 μL and the sample volume is dictated by its water concentration being between 30 and 300 μL. This generates a lower quantity of residue and helps maintain environmental quality while lowering the cost per determination.

The system is isolated from its surroundings avoiding contact of the samples with external moisture and the samples are presented to the system without being exposed to ambient humidity. This certainly helps to improve the accuracy of the water determination.

The proposed titrator is an example of a flow-batch system in which the batch characteristic of the monosegmented concept is exploited to the extreme. The system presents reduced dimensions because homogenization, after titrant additions, is achieved by cycling instead of carrying the monosegment through a long manifold. Also, this approach permits the use of electrochemical monitoring of the monosegment titration because the cell can be maintained under stable conditions with the electrodes always in contact with the titrated solution.

4. Conclusions

The proposed system exploits the most important characteristic of the monosegmented concept to produce a mechanized titrator for water determination in organic solvents by the Karl Fischer method. The main advantages of this titrator are: its size; its ability to easily keep the sample and reagents free of contamination from ambient moisture; its independence of the precision of peristaltic pump flow rates; its capability to perform true titrations that preclude the use of analyte standards; its use of low volumes of sample (typically 30–300 μL) and Karl Fischer reagent (typically 100 μL), contributing to reduce both the cost of analysis and production of residue, and its use of electrochemical techniques to follow the titration progress and for end point location.

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