TECHNICAL NOTES

Automation of Karl Fischer Water Titration by Flow Injection Sampling

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INTRODUCTION

Karl Fischer (K-F) titration is the most widely used method for the routine determination of water in samples. There are drawbacks associated with the original K-F method: unpleasant pyridine-based reagent, slow reaction, poor precision, and interferences. Many improvements on the K-F titration method have been made since Karl Fischer first published the method in 1935, including the development of a new titration apparatus and pyridine-free reagent (*1*, *2*). The drawbacks can be minimized or overcome by choosing appropriate reagents and instrumentation.

One application in need of development is the automation of K-F titration. In many chemical processes, it is often desirable to measure water content of a liquid process stream on-line. In a laboratory the usual practice of using commercial K-F titrators (*1*, *2*) requires manual and sequential determinations that are both labor intensive and prone to error; therefore, it is advantageous to automate the water analysis to handle a large quantity of samples.

Various attempts have been made to develop an automatic K-F titration system since 1980. The flow injection analysis approach (*3*–*7*) showed the following problems: poor sensitivity, as compared to that obtained with the conventional K-F method; large variation in results caused by matrix or blank effects; unsatisfactory results for water concentration below 0.03%; requirement of standards that need to be validated by another method. The recent titration cell approach (*8*) resulted in an improved precision, but the feasibility of this approach for automation has yet to be demonstrated. In yet another example (*9*), adding a sample changer to a volumetric titrator allowed for the unattended analysis of laboratory samples. However, this system is not suitable for on-line monitoring or for hygroscopic samples due to its vulnerability to atmospheric moisture.

Many commercial K-F titrators can measure water coulometrically over a wide range, from micrograms to milligrams (*2*); their drawback is the sample introduction system, which mostly is a manual operation. We automated such a manual system by recirculating the anode reagent from a coulometric K-F titrator through a mechanically controlled loop sampling valve. The recirculation serves as a means for transporting and mixing the sample to the titration cell. The active reagent, iodine, is generated coulometrically while water is being titrated. The end point is reached when water is consumed. The integrity of the K-F titrator is kept. Although this novel approach to automation is based on a flow injection sampling technique, the end point determination using the K-F titrator differs from the classical flow injection analysis (*3*–*7*) or the continuous flow analysis (*10*, *11*), which mainly is a kinetic-based determination.

This automatic sampling system is easily coupled to existing titrators for either on-line or laboratory application. The automation also improved the precision.

EXPERIMENTAL SECTION

Reagents were industrial grade *N*-methyl-2-pyrrolidone (GAF Corp.), anhydrous methanol (Fisher Scientific), 5A molecular sieves (Alltech Associate), and HYDRANAL Coulomat A (anode reagent) and Coulomat C (cathode reagent) (Crescent Chemical Co.) for the coulometric K-F titrator.

Instrumentation. The flow diagram for the automated K-F titrator is shown in Figure 1. All equipment was obtained from commercial sources and comprises the following items: a coulometric K-F titrator, Aquastar C2000 equipped with an AQI-601 communication board (EM Science); an autosampler, Precision Sampling Model LC241 (Dynatech); a double-piston pump (Eldex Lab, Inc.); a six-port sample injection valve with a pneumatic actuator (Models 7010 and 5701, Rheodyne, Inc.); three sample loops with nominal volumes of 50 μL, 100 μL, and 1.0 mL (Alltech Associate); a three-way switching valve with a pneumatic actuator (Models 5301 and 5300, Rheodyne, Inc.); two digital valve interfaces (Valco Instruments Co., Inc.); an integrator as a remote time controller (Model 4270, Spectra-Physics); an air pressure of 40 psig for both actuators; tubing of Teflon fluorocarbon resin, $^1/_{16}$ in. o.d., 0.5 mm i.d. of various lengths for all liquid communication. The anode reagent was circulated at 5 mL/min from the coulometric K-F titration cell to the six-port injection valve and then back again to the cell by a pump through Teflon tubing.

For *laboratory automation*, the sample inlet port of the injection valve was connected to an autosampler. The K-F titrator and the autosampler were connected to allow automated operation. The communication between the titrator and the autosampler was arranged so that when the background reading of the titrator was stable, the titrator sent a signal to the autosampler which initiated the sampling cycle. First, the sample flushed through the loop; next, the injection valve made the injection, and the titrator started the titration. The titrator printed out the water content at the end of the titration and sent a signal to the autosampler for the next sample cycle.

For *on-line monitoring*, the sample inlet port of the injection valve was connected to a three-way switching valve, which was connected to a circulating sample stream from a process or a sample holding tank (a multistream selection valve can be used for a multichannel sample). The valves and the K-F titrator were in communication by a remote time controller, which directed the valve switching to allow automated operation. The communication among the titrator and the valves was arranged so that when the background reading of the titrator was stable, the titrator sent a signal to the remote time controller which directed the switching valve to divert a sample through the loop, the injection valve to make the injection, and the titrator to start the titration. The titrator printed out the water content at the end of the titration and waited for a selected time interval for the next sample.

Sample Loop Calibration. Two methods were used to calibrate the volume of the sample loops: the first by known addition and the second by comparison with a known volume. A series of water in methanol standards were prepared for the known addition test. The water contents measured by the automated valve system were plotted against the amount of water added (Figure 2). The slope is the calibrated loop volume, which we found to be 55 μL for the nominal 50-μL loop. For the known volume method, a methanol sample was analyzed for water by the automated valve system and by manually delivering a known syringe volume to the K-F titrator. The known volume delivered manually by syringe was also verified by the delivered weight. A water content of 278.8 μg was obtained by an autosampler using the nominal 50-μL loop. The same sample gave a water content of 253.2 μg/50 μL by syringe loading. The ratio 278.8/253.2 is the correction required to calibrate the loop volume. The resulting

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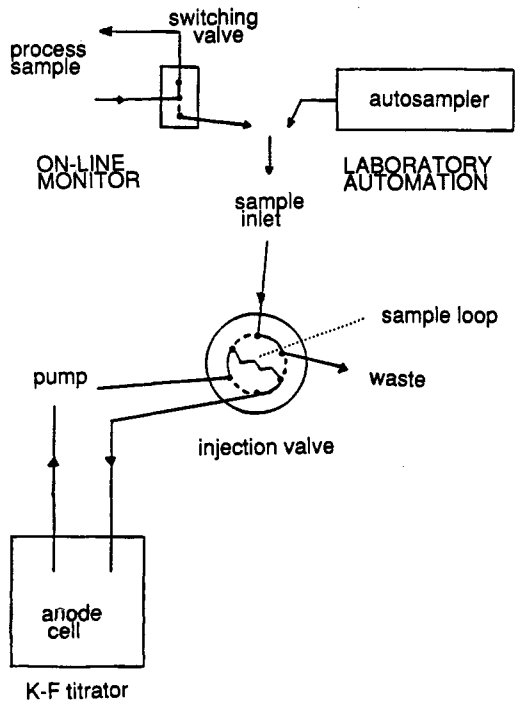

Figure 1. Schematic diagram of the automated Karl Fischer titration system. For laboratory automation, the injection valve is connected to an autosampler. For on-line monitoring, the injection valve is connected to a switching valve.

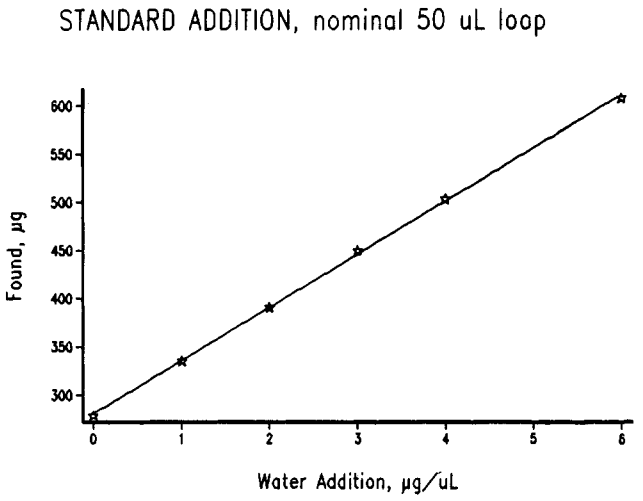

Figure 2. Loop calibration by a standard addition test. Known amounts of water were added to the water/methanol standards; water content was determined by lab automation with a nominal 50-μL loop. The linear fit slope of 55 μL is the measured loop size. ($y = 54.95x + 280.8$; $R^2 = 99.95\%$; root MSE = 2.864.)

volume of 55 μL calculated is statistically equivalent to that obtained by the standard addition method. Two sample loops with nominal volumes of 100 μL and 1.0 mL were calibrated by the known volume method and found to be 103 μL and 1.00 mL, respectively.

RESULTS AND DISCUSSION

The coulometric K-F titration method is considered an absolute measurement. Calibration is not necessary. The accuracy of the coulometric K-F titrator was checked before and after each set of experiments by manually injecting 2.0 μL of pure water with a 5-μL syringe. A recovery of 100 ± 3% (or a reading of 1940–2060 μg of water, including dosing error) indicated that the titrator was in good operating condition and that the data obtained were valid.

Laboratory Automation. The automated system was evaluated by measuring water in *N*-methyl-2-pyrrolidone (NMP). Twenty sealed vials containing NMP were loaded onto the autosampler and analyzed automatically. The 55-μL loop was used. The average water content was 140.9 ± 1.8 μg for 20 replicated samples. The water concentration was calculated to be 0.250 wt % with a relative standard deviation of 1.3% based on a density of 1.026 g/mL for NMP.

For comparison, a sample of methanol with a nominal water content of 5.0 mg/mL was analyzed for water by using manual syringe loading and by using the autosampler. A concentration of 5.06 mg/mL with a relative standard deviation (RSD) of 2.8% ($n = 9$) was obtained by using 50-μL-syringe loading. A concentration of 5.07 mg/mL with a RSD of 1.0% ($n = 9$) was obtained via the autosampler using the 55-μL loop.

The automated method offered three advantages over the manual operation: fixed-loop operation eliminated human error and improved precision, the closed system reduced interference from atmospheric moisture, and automation increased productivity by allowing unattended analysis.

On-Line Monitoring. To evaluate on-line monitoring suitability of the system, a liquid sample was placed in a capped bottle, which simulated a process holding tank. The sample was circulated at 3–5 mL/min from the bottle to the switching valve and back to the bottle. Sample-loading duration (switching time) was chosen to allow three sample volumes to flush through the injector loop to prevent carryover; a loading duration of 1 min was used with a 1.0-mL loop and flow rate of 3 mL/min. The system was programmed through the remote time controller to allow automated sampling at a chosen rate, for example, every 30 min or whenever the background of the titrator was ready for receiving sample.

The methanol sample with a nominal water content of 5.0 mg/mL used in the laboratory automation was tested again. A concentration of 5.04 mg/mL with a RSD of 1.0% ($n = 10$) was obtained by manually injecting 100 μL from a 250-μL syringe. The same sample was then monitored on-line every 2 min by using the 103-μL loop, and a water content of 5.05 mg/mL with a RSD of 0.13% ($n = 15$) was found.

A sample of dry methanol was used to check the injection valve with the 1.00-mL loop. The sample was monitored on-line whenever the titrator was stable and ready for sample. The coulometric current was set at a slow rate of 107 mA. Ten data were obtained in 20 min, and the average water content was 290.7 μg/mL with a RSD of 0.3% ($n = 10$). The water content was also determined by manually injecting 1.00 mL and using a 2.00-mL glass syringe. The average result was 290.5 μg/mL with a RSD of 1.4% ($n = 10$). Again, a better precision was obtained by automation.

To demonstrate the effectiveness of this apparatus as an on-line process monitor, the drying of a bottle of wet NMP by molecular sieves was monitored on-line every 30 min by using the 103-μL loop. A total of 140 samples were measured consecutively for 70 h. A portion of the data is shown in Figure 3. As can be seen, before the molecular sieves were added, the water concentration was stable at 290 ± 1.1 μg/103 μL over the 10-h analysis time. After the molecular sieves were added, the water was absorbed rapidly in the first 10 h and slowly thereafter; an equilibrium value of 28.3 μg was reached after 40 h. The average concentration was 28.3 ± 0.46 μg/103 μL for the final 6 h. The advantages offered by the automated on-line analysis are apparent: the process can be closely monitored and human error can be eliminated, thus, greatly improving operational safety, productivity, and the quality of results.

The combination of a coulometric K-F titrator and loop sampling has another advantage over the conventional method: more sample can be analyzed per reagent charge. This is because the liquid volume in the cell does not change upon analysis, and the titrator cell, therefore, can be filled to its

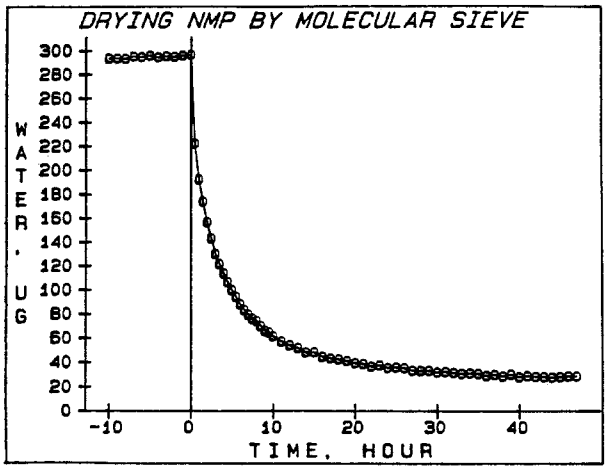

Figure 3. On-line monitoring of the water content in *N*-methyl-2-pyrrolidone. The molecular sieves were added at time 0. A 103-μL sample was titrated for water every 30 min.

capacity with K-F reagent. Two reasons make this practice possible: one the active reagent, iodine, is generated coulometrically in situ and does not have to be added; two, for every sample added to the cell, an equal volume of the liquid in the cell is flushed away. By the conventional method, the sample capacity or the number of analyses is limited by the head space of the cell. For example, the sample capacity cannot exceed 50 mL if 150 mL of K-F reagent is charged into a 200-mL cell; thus, one can expect a maximum of 50 determinations for a 1.0-mL sample size. In comparison, by the loop sampling, 200 mL of the K-F reagent can be charged into the 200-mL cell and more than 50 mL of sample can be added. Clearly the number of analyses also depends on the reagent strength, and the reagent strength is diminishing with increasing sample volume and sample water content. To maximize the number of analyses for each reagent charge, one should choose the smallest sample loop size applicable to the sample water content, the desired accuracy, and the K-F titrator used.

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Laser-Enhanced Ionization Spectroscopy in an Extended Inductively Coupled Plasma

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INTRODUCTION

Laser-enhanced ionization (LEI) spectroscopy has been proven to be a very sensitive trace element technique. Excellent reviews on LEI are provided by Travis and co-workers (*1*, *2*), by Green (*3*), and recently by Axner and Rubinsztein-Dunlop (*4*). The technique involves selective photoexcitation of analyte atoms by laser radiation, followed by collisional ionization of the excited atoms in the atom reservoir. The ion increase is detected by measuring the current change at an electrode and is proportional to the analyte concentration. The electrode designs and arrangements in atom reservoirs have been reviewed (*1*-*4*). Since LEI detection is nonoptical, problems associated with laser radiation scattering and light collection efficiency are not important, and the possibility of nearly 100% ion collection efficiency allows the detection of very low analyte concentrations. The detection limits of LEI in flames are comparable to those obtained with graphite furnace atomic absorption spectroscopy (*4*).

Flames are inexpensive, simple, reproducible, and readily available in most laboratories and provide an excellent collisional thermal medium; flames are most commonly used as atom reservoirs in LEI experiments. Standard burners used in analytical flame atomic spectroscopy are employed. These include the premixed 5-cm slot burner (*5*), the premixed 10-cm slot burner (*6*), the premixed capillary burner (*7*), and the total consumption burner (*8*). These burners are generally equipped with a pneumatic nebulizer, which transports a sample solution into the flame in the form of small droplets. The ability for a flame to produce free sample atoms depends on the fuel and oxidant used. The acetylene–air flame is the choice for most elements (*4*). The cooler hydrogen–air flame is useful for elements with low ionization potentials, such as rubidium. The hot acetylene–nitrous oxide flame is effective for refractory elements such as vanadium and titanium. The combustion products of flames, however, may hinder some of the spectral regions for successful implementation of LEI. Nonflame atomizers such as the graphite furnace also have been used (*9*).

The inductively coupled plasma (ICP) has long enjoyed popularity as an efficient atom reservoir for atomic emission (*10*) and atomic fluorescence (AF) (*11*) spectroscopy. Its effectiveness is partially attributed to the high temperature inert argon atmosphere. The ICP also is used as an ion source for mass spectrometry (*12*). The low detection limits (*11*) obtained with ICP-AFS excited by hollow cathode lamps, lasers and ICP have led one to believe there is a high popu-

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