# Automated Gravimetric Management of Solutions

# Part 2.* Automated Gravimetric Approach to Direct Potentiometry and Kappa Number Determination

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**The high-performance microcomputer controlled gravimetric burette described in Part 1 has been employed to automate some routine analytical procedures. A direct potentiometric determination of fluoride ions in drinking water was developed to include an automatic calibration step, matrix adjustment and sample determination. Also the complex and cumbersome titrimetric procedure for determination of the kappa number (lignin content) in paper pulp, has been automated by using the gravimetric unit and biamperometry. In this last instance, the automatic standardization of the solutions employed in the determination and the complete automation of the recommended kappa number determination procedure, allows a significant reduction in the amount of reagent consumed. The gravimetric approach to these procedures reveals that the same performance is achieved in terms of precision and accuracy when compared with classic volumetry while the cost associated with the automation decreases owing to the use of the same unit to attain automatic management of up to three different solutions.**

*Keywords: Automated gravimetric burette; fluoride determination in drinking water; kappa number of paper pulp; automation of biamperometric titrations; direct potentiometry*

## Introduction

The use of volumetric apparatus is a common place in the routine laboratories. The automation of analytical procedures involving solution manipulation had been achieved by the use of automatic comercially available volumetric dispensing devices. However, the modern digital electronic balance and its capability of communication with microcomputers through a simple RS-232 serial interface has created the possibility of incorporating the gravimetric management of solutions in the laboratory.

Perhaps the most important reason for evaluating gravimetric procedures for routine determinations is in the search for automation for the modern analytical laboratory. Once the procedures have been automated, the advantages of the conventional volumetric apparatus, such as easy manipulation, will no longer exist and the inherent advantages of the gravimetric approach predominate.

A complete replacement of volumetric manipulation of solutions by gravimetric manipulation would require a complete change of, for example, the usual concentration units, some definitions and standard analytical procedures. Therefore, it is more probable that both approaches will co-exist in the laboratory even if gravimetric devices become available for routine use.

In a previous paper the construction of a high-performance microcomputer controlled gravimetric burette was described.[1] The device, characterized by its versatility and the inherent use of the microcomputer, elects the gravimetric burette to be employed in the automation of routine analytical procedures.

The automation of direct potentiometric procedures using volumetric dispensing devices has been described in the literature.[2,3] These automatic procedures, however, were intended only to automate the sample determination steps. The adjustment of the medium and the automation of the electrode calibration procedure have not been described. At most, some procedures can perform the calibration if the user introduces a set of pre-prepared standard solutions.

Potentiometry is widely used for determination of $F^-$ in a number of different samples[4-7] and the method is recommended as standard for drinking water quality control.[8] Some potentiometric instruments have been developed specifically for $F^-$ determination by customizing the way in which the concentration units are expressed and minimizing the sample and standard solutions manipulation. Again, the degree of automation found in commercial instruments is low and, in practice, only data transformation from the obtained potential values to $F^-$ concentration units is achieved.

The kappa number ($K$) is a parameter associated with the lignin content of paper pulp and is employed in the paper factory to control the bleaching process. The definition of the $K$ is very restrictive and empirical.[9] The $K$ value is defined as the volume (in ml) of a $0.02$ mol $l^{-1}$ potassium permanganate solution consumed by one gram of dry pulp under well defined conditions (10 min reaction time, 25 °C and at fixed initial $KMnO_4$ concentration and medium acidity). The final result is corrected to 50% consumption of the added permanganate. Pulp processing plants are adapted to this definition and a modification would not be acceptable. The analytical procedure recommended to obtain the $K$ value is complex and involves the use of three reagents whose quantities should be controlled. The procedure requires the determination of the $KMnO_4$ remaining in a reaction with the lignin under restricted well defined conditions including reaction time, initial concentrations and temperature. The $KMnO_4$ remaining is found indirectly by adding an excess of $I^-$ and titrating the $I_2$ formed with standard $Na_2S_2O_3$ solution. For manual procedures, the use of starch as the end-point indicator is recommended[10] while the biamperometric technique can be used for the automated instrumental approach.

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* For Part 1, see ref. 1.

The automation of the $K$ determination is a challenge, not only in view of its complexity, but also in view of the necessity to apply the gravimetric approach in the determination of a parameter well accepted in the industry and fully defined in volumetric terms.

The present paper describes the use of the gravimetric instrumentation previously developed[1] to implement automatic procedures for direct potentiometry and titrimetric procedures that require complex operations such as kappa number determination. These procedures were chosen to illustrate the fact that, with some advantages, the automatic gravimetric management can compete with the volumetric approach without serious modifications to the routines carried out in the analytical laboratory and that volumetric and gravimetric approaches can co-exist by retaining well established volumetric definitions while performing the analytical procedures using gravimetric systems.

## Experimental

### Gravimetric Systems

Fig. 1 shows a schematic diagram of the gravimetric aparatus employed to automate the direct potentiometric and kappa number determination procedures. For the direct potentiometric determination of $F^-$ in drinking water, the burette flasks (1–3) and the external stock flasks (I–III) contain, respectively, the buffer [TISAB (NaCl–*trans*-1,2-diaminocyclohexane-$N,N,N',N'$-tetraacetic acid), Orion, Cambridge, MA, USA Cat No. 94-09-00] for pH, ionic strength and $F^-$ release from metal complexes, a $10^{-3}$ and a $10^{-2}$ mol $l^{-1}$ $F^-$ standard solution. An electrode selective to $F^-$ ions (Radelkis, Budapest, Hungary; Model OP-F-07113) and a Ag/AgCl double junction reference electrode were employed with a potentiometer (Micronal, São Paulo, Brazil, Model 360).

For kappa number determination the magnetic stirrer shown in Fig. 1 was replaced by a mechanical one to keep the pulp dispersed in the solution. Flasks 1–3 and I–III contained, respectively, a 0.15 mol $kg^{-1}$ $KMnO_4$ solution, a 0.20 mol $kg^{-1}$ $Na_2S_2O_3$ solution and a 0.5 mol $kg^{-1}$ NaI solution. An ammeter (Radelkis, model OP-508) and a ring combined platinum electrode were employed to monitor the biamperometric titrations. A potential difference of 150 mV was applied to the electrodes.

An IBM-386 compatible microcomputer was employed to control the gravimetric burette, to execute the analytical procedure and to perform data acquisition and treatment. Detailed description of the gravimetric burette and of the purpose-built interface can be found in Part 1.[1]

In addition to the previously reported main sub-programs for the control of the gravimetric unit, a new sub-program has been written to be used for an exact transference of mass as requested by the user. This sub-program, given in the Appendix, became necessary as the $K$ determination requires that the lignin reacts in a concentration of $KMnO_4$ pre-defined by the standardized methodology.[10]

### Direct Potentiometric Procedure for $F^-$ Determination in Drinking Water

The procedure for $F^-$ determination in drinking water consists of two parts. The first is an automated calibration of the potentiometric system. Water (10.00 ml) is added from a beaker to the gravimetric/potentiometric system by which 1.300 g of TISAB is added. Standard solutions of $F^-$ are subsequently prepared in the same flask under software control by calculating the mass of the standard stock solution necessary to reach concentrations values near those selected by the user. To express the concentration in mol $l^{-1}$, the density of the diluted NaF stock standard solutions are assumed to be 1.00 g $ml^{-1}$ and the density of the TISAB needs to be known. The program automatically controls and selects the standard stock solution necessary to reach the requested $F^-$ concentration. When the amount of solution necessary exceeds 1.0 g, the more concentrated solution is employed. For a five-point calibration in the range of $10^{-3}$–$10^{-5}$ mol $l^{-1}$, the dilution of the initial TISAB solution present in the beaker, caused by the standard solution addition, was assumed not to cause a significative change in ionic strength.

After each addition of $F^-$ solution, the potential of the cell is read through the interface and stored on disk for subsequent use in fluoride determinations. For determination of $F^-$ in drinking water, the same initial volume (10.00 ml) of sample is introduced into the system, adding the same mass of TISAB as that employed in the calibration step and the potential is recorded. The linear calibration equation, obtained by the least-squares-method and stored in the computer, is used to obtain the concentration of $F^-$.

### Automation of Biamperometric Titrations

The titrations for automatic kappa number determination were followed by biamperometry. The procedure to perform biamperometric titration of the $I_2$ with sodium thiosulfite is widely employed in routine determinations. When the $I_2$ content is monitored, the technique named dead-stop can be used to find the end-point of the biamperometric titration. To automate this procedure the behaviour of the current as a function of the thiosulfate addition was observed for a typical titration. Three threshold values of current and its final residual value were selected as shown in Fig. 2.
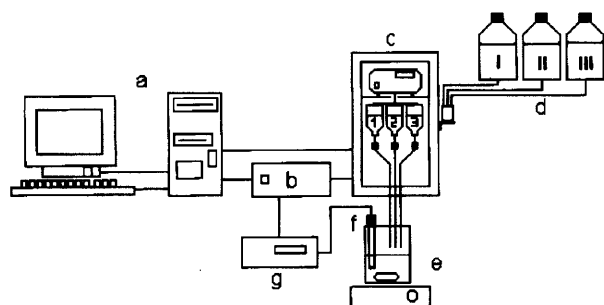


**Fig. 1** Automatic gravimetric system as assembled for potentiometric fluoride determination in drinking water. a, microcomputer; b, interface; c, gravimetric burette; d, external reservoir flasks; e, magnetic stirrer; f, fluoride selective electrode; g, potentiometer. For kappa number determination the magnetic stirrer was replaced by a mechanical one and the potentiometer by an ammeter. A double ring platinum electrode was employed for the biamperometric titrations.
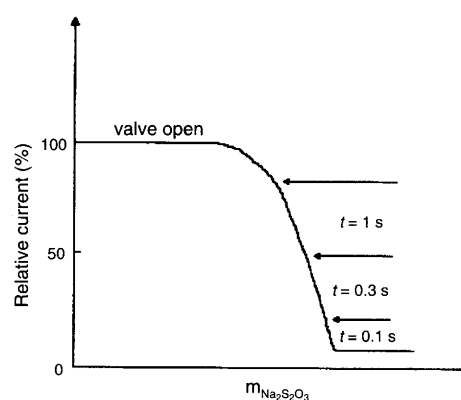


**Fig. 2** Typical titration curve obtained in the kappa number determination showing how the software manages the titrant addition as a function of the measured current in order to find the end-point of the titration.

The titration is initiated by continuously delivering the $Na_2S_2O_3$ solution to the titration flask. The current is recorded and when the first threshold value is reached the titrant addition is stopped. The software starts to add the reagent in a time-controlled routine in which the value is opened for 1 s intervals. When the current reaches the second threshold value the software reduces the time interval to 0.3 s and values of current below the last threshold causes the time interval to be reduced further to 0.1 s. This procedure allows the end point, found when the current reaches its residual value, to be attained as fast as possible without the risk of addition of an excess of titrant. Typical titrations can be performed in about 3 min by using this iterative procedure.

### Automatic Determination of the Kappa Number

The determination of the kappa number requires the use of standard solutions of $KMnO_4$ and $Na_2S_2O_3$. The gravimetric system provides two automatic standardization procedures for those solutions based on biamperometric titration. The user can select the procedure and whether the system is to perform a duplicate or triplicate standardization.

The $Na_2S_2O_3$ solution should first be standardized. The user presents to the system a known volume (typically 20.00 ml) of a primary $K_2Cr_2O_7$ standard solution (about $4.0 \times 10^{-3}$ mol l$^{-1}$) prepared in 0.5 mol l$^{-1}$ $H_2SO_4$. The system adds a sufficient mass of the NaI solution and initiates the titration of the $I_2$ formed using the $Na_2S_2O_3$ solution following the procedures described above. The correct concentration of the $Na_2S_2O_3$ solution is calculated and stored in a data file used by the system.

Once the concentration of the thiosulfate solution is known, the $KMnO_4$ solution can be standardized. About 50.0 ml of a 0.2 mol l$^{-1}$ $H_2SO_4$ solution is introduced into the gravimetric system. Under computer-control, a mass of about 1 g of the $KMnO_4$ solution is added to the acid solution followed by a sufficient mass of NaI solution. Again the $I_2$ formed is titrated employing the $Na_2S_2O_3$ solution previously standardized. The $KMnO_4$ concentration is stored to be used in the kappa determination. In accordance with the recommendations for Good Laboratory Practice (GLP) the software checks periodically the date of the last standardization effected, for each solution, and alerts the user to the need for new standardization.

The determination of $K$ is carried out by dispersing a moist mass of pulp (between 0.25 and 1.5 g for kappa numbers in the range 18 to 2, respectively), the water content of which should be known, in 100.0 ($\pm$ 0.5) ml of a 0.2 mol l$^{-1}$ $H_2SO_4$ solution. The suspension is maintained under mechanical agitation during all the analytical procedure. The three delivering tubes of the gravimetric burette are placed deep in the acidic pulp suspension and the program is started. A suitable mass (about 1.0 g) of the $KMnO_4$ solution is added to the suspension by employing the addexactmass sub-program in order that its concentration is in agreement with the recommended value defined in the conventional procedure.[10] The software calculates the mass (g) to be added ($m_K'$) by using the equation:

$$m_K' = \frac{0.202}{c_{KMnO_4}} \tag{1}$$

where $c_{KMnO_4}$ is the concentration (mol kg$^{-1}$) of the permanganate solution contained in flasks 1 and I in the gravimetric burette. After the addition, the reaction between permanganate and the lignin present in the sample is allowed to occur for the 10 min recommended time interval.[10]

After the reaction time has elapsed the system adds an excess of NaI (about 3.5 g) and starts the titration of the $I_2$ formed. When the titration is finished the user is prompted to enter with the dry mass ($m_D$) of the pulp employed in the determination.

The final value of the $K$ is calculated by the software employing the following equations. The mass of the $KMnO_4$ solution actually added ($m_K$) is converted to the volume of 0.02 mol l$^{-1}$ $KMnO_4$ solution ($V_K$) by the equation:

$$V_K = \frac{c_{KMnO_4} \, m_K}{0.02} \tag{2}$$

The volume of 0.02 mol l$^{-1}$ $KMnO_4$ solution remaining ($V_R$) after reaction with the pulp is found by:

$$V_R = 10 c_{Na_2S_2O_3} \, m_T \tag{3}$$

Where $c_{Na_2S_2O_3}$ is the concentration of the thiosulfate solution (mol kg$^{-1}$) and $m_T$ is the mass of this reagent employed in the titration of the $I_2$ formed. The volumetric percentage of the $KMnO_4$ ($V_c$) solution consumed in the reaction if given by:

$$V_c = \frac{V_K - V_R}{V_K} \times 100 \tag{4}$$

The $V_c$ value is employed in the calculation of the kappa number ($K'$) corrected for a 50% consumption of the $KMnO_4$ solution, as required by the definition of the standard $K$ determination:[10]

$$\log K' = \log \frac{V_K - V_R}{m_D} + 0.00093 \, (V_c - 50) \tag{5}$$

The determinations were made with solutions at the laboratory ambient temperature of 25 °C. However, if a different temperature ($T/$°C) is used the software can correct the $K$ value by using the equation:[10]

$$K = K' \, [1 + 0.013 \, (25 - T)] \tag{6}$$

### Results and Discussion

Table 1 shows results for determinations of F$^-$ in drinking water obtained by conventional potentiometry and by the proposed automatic procedure. Statistical analysis of those results reveal that the F$^-$ concentration obtained by the proposed method ($y$) is related to the concentration found by the standard method ($x$) by the equation: $y = 0.017(\pm 0.984) + 0.976(\pm 0.255)x$. The correlation coefficient is 0.938 and the standard error of the estimate is ($\pm 0.177 \times 10^{-5}$) mol l$^{-1}$ of F$^-$. Linear calibration curves were obtained for the gravimetric calibration procedure in the concentration range of use in regarding the determination of F$^-$ in drinking water ($10^{-3}$–$10^{-5}$ mol l$^{-1}$). The calibration of the potentiometric system as proposed is effected without any intervention of the user and, therefore, is less prone to human error. The calibration can be performed in only 6 min if a five-point calibration is requested. Re-validation of the calibration can be processed automatically by once again placing the 10.00 ml of water in the gravimetric system and ordering this operation from the main menu of the program. The system will

**Table 1** Results for determination of fluoride in drinking water by the conventional and proposed methodology. Samples were taken from different regions of the city of Campinas.

| Sample | Conventional method | Proposed method |
|---|---|---|
| | Fluoride concentration/ 10$^{-5}$ mol l$^{-1}$ | |
| 1 | 4.0 | 3.9 ($\pm$0.2)* |
| 2 | 3.8 | 3.6 |
| 3 | 4.1 | 4.1 |
| 4 | 3.5 | 3.7 |

\* Standard deviation in parentheses ($n = 5$).

produce a standard whose concentration is in the middle of calibration curve, will predict its concentration by using the stored calibration parameters and will alert the user if the result differs from the one expected by an amount defined in the setup of the program. Determinations are performed in 40 s in a procedure that includes the adjustment of the medium by the addition of TISAB. The only step not automated in the gravimetric procedure is the electrode cleaning between samples although it should be considered that for routine purposes, where the concentration of the samples does not change significantly, the washing procedure should not be necessary.

Table 2 shows results obtained for the determination of the kappa number by the automatic gravimetric method and by the conventional method.[10] The range of $K$ values is that found in routine determination performed in cellulose paste factories for pulps before ($K \approx 18$) and after ($K \approx 2$) bleaching. The results, obtained by the gravimetric method ($y$) are related to those

found by the standard kappa determination procedure ($y$) by the equation: $y = -0.0659(\pm 0.0889) + 1.0039(\pm 0.0076)x$. The correlation coefficient is 0.9998 and the error of estimate is $\pm$ 0.14 kappa units. The precision obtained by the automatic method is within reported values for the manual volumetric method.[9] However, a reduction of tenfold in reagent consumption has been achieved by use of the gravimetric method in comparison with the conventional one. The sequential determination of the $K$ here proposed has the disadvantage that the standard procedure requires a 10 min reaction time before the remaining permanganate can be determined. Therefore, the sequential throughput is about 5 samples per hour. The titration of the $I_2$ formed in the last step of the automatic $K$ determination procedure takes about 2 min. Therefore, if a parallel processing of samples is adopted the throughput could be increased to the limit of 30 determinations per hour.

The use of the gravimetric system previously developed[1] in the automation of the potentiometric determination of $F^-$ and for K determination provides good examples of the versatility of the gravimetric approach to the management of solutions and shows that even parameters fully defined in volumetric terms and of routine use in industrial quality control (such as the $K$ number), can be automatically determined by the gravimetric system.

The search for automation of analytical procedures has produced a leveling effect on the volumetric and gravimetric methods causing the latter to become competitive in the management of solutions in the analytical laboratory. The future of gravimetric automatic systems in the routine laboratory appears, based on the results reported previously[1] and on this paper, to be limited only by the production of commercial instruments.

**Table 2** Results obtained for determination of the kappa number of cellulose paste by the conventional volumetric and the proposed automatic method. Samples were collected in the pulp production process on different days, before and after the bleaching treatment

| | Kappa number | |
| Sample | Volumetric method | Proposed method |
| --- | --- | --- |
| 1 | 2.18 | 2.31 |
| 2 | 11.81 | 11.86 |
| 3 | 2.12 | 2.02 |
| 4 | 18.25 | 18.25 |
| 5 | 17.83 | 17.80 (±0.12)* |
| 6 | 2.33 | 2.10 (±0.05)* |

* Standard deviation in parentheses ($n = 5$).

## Appendix

### *LISTING 1*

This sub-program intended to add a mass (mpg) that is as close as possible to that requested by the user. The solution is delivered from flask np%. The mass actually added is returned to the calling routine as madp. The factor fm defines a fraction (typically 90%) of mpg for the initial one shot mass addition. ta is a short (typically 0.5 s) time interval for valve aperture aimed to approximate as close as possible the actually added mass to the required mass. See ref. 1 for additional information on the software for the gravimetric unit.

```
SUB addexactmass (mpg, fm, ta, np%, madp)
      mpgi = mpg * fm
      CALL addmass (np%, mpgi, madp) ' adds a fraction of the requested mass
            deltamass = mpg - madp 'mass to be still added
                  CALL readbalance (flaginst%, mass, stb) 'reads the balance
                        mi = mass
      WHILE madd < deltamass      'this loop will approximate the requested mass
                  a = timer        'as close as possible
            CALL valveon (np%)
                  WHILE (timer − a) < ta : WEND
            CALL valveoff (np%)
            CALL readbalance (flaginst%, mass, stb)
                  madd = mass - mi
      WEND
      madp = madp + madd
END SUB
```

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