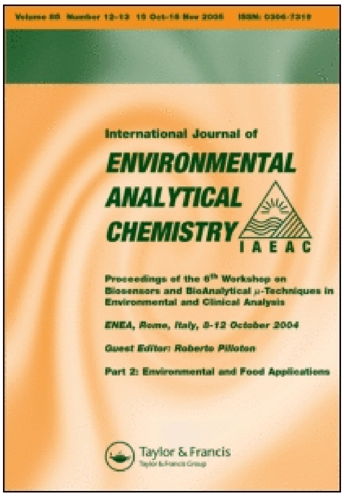

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AUTOMATED SYSTEM FOR THE COULOMETRIC DETERMINATION OF CHLORIDE IN WATERS

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An automatic system for coulometric measurements controlled by an IBM PC-compatible computer was developed. The system is made up of commercially available instruments and interfaces and is controlled via software designed for coulometric titrations applied for general purposes (precipitation, acid-base reactions) which can be used by unskilled workers through user-friendly menus.

The performance of the system was studied by applying it to the determination of chloride with eletrogenerated silver; it yielded determination limits of about 4 μeq—clearly lower than those afforded by the Mohr method—, good reproducibility (RSD < 3%) and good accuracy (within 1%). The system allows the fully automated analysis of 13 samples in roughly 1 h and was successfully applied to the determination of chloride in various types of water.

INTRODUCTION

The advent of personal computers, and of the IBM-PC standard in particular, has opened rather promising prospects to the automation of analytical laboratory procedures. The ease with which computers can be programmed in high-level languages and the increasing accessibility of instrumentation for control by computers has compelled researchers to re-approach a number of instrumental techniques. Thus, formerly time-consuming, sluggish or highly sophisticated techniques can now be advantageously applied, provided appropriate software is developed in order to minimize the need for human intervention. Among such techniques are constant-current coulometric titrations. While they have always been praised academically for their outstanding features, they have scarcely been used in routine laboratory analyses. The lack of popularity of coulometric titrations is also reflected in the rather small number of references to them in Chemical Abstracts compared to other instrumental alternatives.

The present work starts a new research line aimed at showing the potential major advantages of the computerized application of coulometric titrations in both research and applied analysis laboratories. One such advantage is that no standardized reagents are required.

A comprehensive search in the literature on automatic coulometric titrators reported over the last decade revealed them to be small in number, but complex to use—they rely on the use of relatively powerful microprocessors which are difficult to interface to available instrumentation and to operate by unskilled workers,[1] or even require the use of the more powerful computers of the Apple family.[2,3] Some other coulometric titrators controlled by non-standard computers have also been marketed by several firms.[4,5]

The great interest in the determination of chloride in various types of water is shown by the usual choice of this anion to demonstrate the virtues of coulometric titrators.[1,2,5,6] However, routine analyses for chloride continue to be addressed by the Mohr method,[7,8] which prompts the need for new, straightforward coulometric titrators requiring no human intervention for the automatic analysis of small numbers of samples. The most important disadvantages of the Mohr method are the narrow pH working range, the need of an important indicator correction and the relatively high limit of determination (3 mg of Cl^-). All these drawbacks can be avoided with the proposed method.

EXPERIMENTAL

Reagents

—Solution 2 M KNO_3 in 2 M acetic acid.

—Standard 0.1 M NaCl solution.

—0.0985 M $AgNO_3$ solution (for Mohr method), standardized with the NaCl standard solution.

All other reagents used were of analytical reagent grade.

Instrumentation

The system developed for the automatic implementation of coulometric titrations consists of the following elements:

—A PC-compatible computer.

—A 14-bit, 16-channel FPC-011 analog/digital converting board from Flytech Technology Co.

—An FPC-046 board, also from Flytech Technology Co., with 16 independent relays.

—A microSAMPLER 2040 autosampler from Crison Instruments SA (Riera Principal 24-26, 08328 Alella, Barcelona, Spain).

—A Crison microBUR 2031 autoburette.

—An AMEL 555 C potentiostat/galvanostat.

—An Ag-plate generating electrode (immersed surface $\simeq 5\,cm^2$) and a Pt ring counter-electrode.

—An Ag/AgCl reference electrode furnished with a salt bridge, and a silver wire or an Orion 94-17A chloride ion-selective electrode as indicator.

The Pt ring electrode was immersed in a 2 M KNO_3 solution, which was brought into electrical contact with the titration cell by means of a salt bridge consisting of KNO_3-saturated agar. The salt bridge of the reference electrode to the solution contained 2 M KNO_3.

The silver plate electrode was made from a thin $5 \times 1 \times 0.2\,cm^3$ silver jewellery plate. Its cost was about $10, most of which was expended on labour. It is rather straightforward to construct and has quite a long useful life, which in turn makes

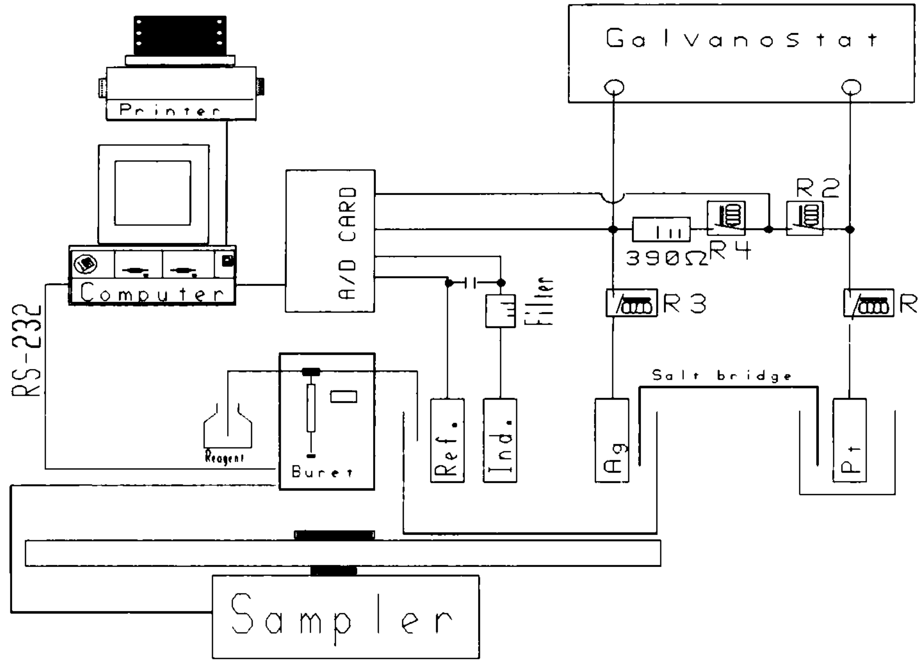


Figure 1 Block diagram of the set-up used.

silver cost per analysis much lower than those typically incurred when using silver nitrate as titrant.

The instrumental set-up used is depicted in Figure 1. Switches R_1–R_4 are computer-controlled relays which allow the current to be passed through the cell. The current is started by closing the circuit at R_1 and R_3 via the computer, so that the generating electrodes are connected to the galvanostat. The current is stopped by switching relays R_1 and R_3 off, and R_2 and R_4 on, with which the electrodes are disconnected from the galvanostat, the current of which is diverted to a 390-ohm electrical resitance. In this situation, the computer measures the potential drop across the resistance by means of the A/D converting board in order to calculate the current intensity yielded by the galvanostat.

The titration curve is acquired through the A/D converting plate connected to the indicator electrodes via an RC filter ($R = 213\,\text{kohm}$, $C = 6.8\,\mu\text{F}$) by using a channel different from that employed to measure the current.

The autosampler, controlled by the computer via its RS-232 interface, allows the automated uninterrupted analysis of up to 13 samples. Finally, the autoburette, also controlled by the computer via its RS-232 interface, allows a sample or some reagent to be added during the analyses.

Software

The instrumentation used was governed and titration curves were acquired with the aid of the purposely written COULOM program, which was entrusted two basic functions, namely, acquisition of the titration curves and data processing.

Acquisition of the titration curves. The program allows three types of titration to be controlled: continuous, fixed-addition and standard-addition titrations.

In the first case, once the current yielded by the galvanostat has been measured, it is passed through the titration cell and data acquisition is started simultaneously, so the current is passed uninterruptedly until the end of the titration.

In the second case, the current is passed for a preset time, after which it is stopped, the indicator electrode is allowed to stabilize and a point of the titration curve is acquired. This process is repeated until the titration is finished.

The third case is similar to the second one, with the exception that the time over which the current is passed to acquire each point is not fixed, but calculated by the program from the evolution of the titration curve: the more distant it is from the equivalence point, the longer such a time is.

The continuous method is the most practical one, because it results in the fastest analyses; however, it is subject to a low systematic error arising from the acquisition of data under non-equilibrium electrode conditions as we will describe in the Results and discussion section.

The program allows the successive analysis of all the samples on the carousel independently, i.e. the working parameters (titration method, end potential, data acquisition rate, etc.) can be suited to the specific requirements of each sample. The program then commands the system to analyse each of the samples according to the specified parameters and, optionally, stores the acquired data on disk and/or processes them to report the results via a printer.

Data processing. The first step involved in processing the acquired data entails smoothing the experimental curve and calculating its first and second derivatives. These computations are done by the Sawitzky–Golay method.[9] Then, the equivalence time is calculated from the maximum of the first derivative of the titration curve, and the sample equivalents are obtained from the equivalence time calculated and the current intensity measured by the computer prior to the analysis. Both the smoothed curve and first two derivatives can be displayed on the computer screen, so that the user can check the accuracy of the calculation and correct it if needed.

Procedure

In each sample cup a known volume of sample containing between 4 and 40 μeq Cl^- is placed, and 10 ml of 2 M KNO_3 in 2 M acetic acid solution, and distilled water are added up to 40 ml. Then, the galvanostat current intensity is set manually and the program is started to analyse the samples.

For greater convenience, the program commands the autoburette to add some distilled water to adjust the final volume before starting the titration of each sample.

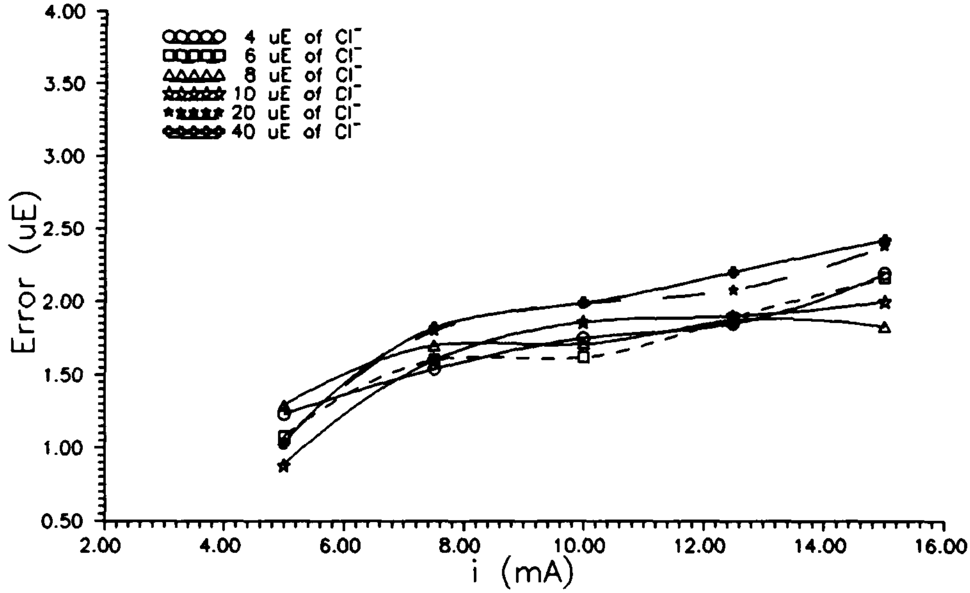


Figure 2 Error (μeq) made in the determination of chloride at different current intensities and analyte concentrations, using a chloride-selective electrode as indicator.

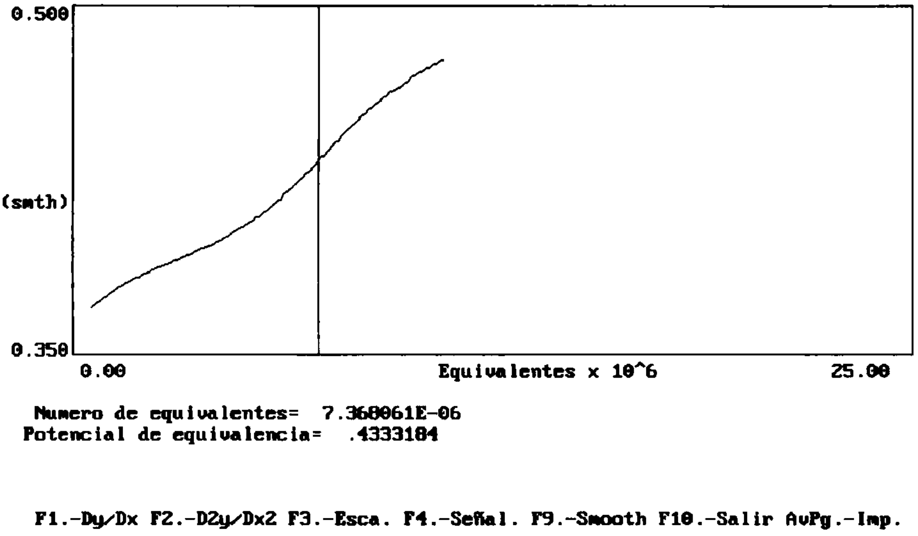
Unless otherwise stated, the results given below were obtained by applying the continuous method at a current intensity of 10 mA.

RESULTS AND DISCUSSION

In order to check the performance of the system at different current intensities and analyte concentrations, we determined the errors made in the analysis of a series of standard chloride ion solutions of different concentration, using various current intensities. All determinations were carried out as described above, using a chloride ion-selective electrode in the continuous fashion.

The absolute errors made in the various analyses are shown in Figure 2, where each point represents the average of the results obtained for four independent samples. As can be seen, the determinations were subject to a systematic error which was essentially independent of the analyte concentration and varied slightly with the generating intensity applied, though it tended to level off at currents above 8 mA.

The systematic error was found to decrease substantially on carrying out analyses in a batchwise fashion and allowing the indicator electrode to stabilize prior to each measurement (which is done using the fixed-addition or the standard-addition titration modes). This led us to believe that the error might arise from a slow response of the electrode in the continuous-operation mode. However,



```
Numero de equivalentes=  7.368061E-06
Potencial de equivalencia=   .4333184


F1.-Dy/Dx F2.-D2y/Dx2 F3.-Esca. F4.-Señal. F9.-Smooth F10.-Salir AvPg.-Imp.
```

Figure 3 Coulomnetric titration curve for 6 μeq of chloride, captured from the computer monitor screen. The vertical line indicates the automatically determined equivalence point. Indicator electrode: chloride-selective. $i = 10\,\mathrm{mA}$.

the time required for each batch analysis was much too long (about 20 min compared with only 5 min in the continuous analyses). Thus, as the error made remains approximately constant (1.8 μeq in excess) and almost independent of the analyte concentration between 8 to 12 mA, we opted for using the continuous method and introducing the appropriate correction in the results.

As an example, Figure 3 shows a screen captured from the computer video monitor corresponding to the automatic continuous coulometric titration of a 6 μeq chloride standard solution, utilizing a chloride ion-selective electrode and a current intensity of 10 mA. The figure shows both the titration curve and the position of the equivalence point which is automatically determined (vertical line). As can be seen, despite the low content assayed—unaffordable by the Mohr method—, the potentiometric curve obtained is quite acceptable. Below the graph, the program presents the number of equivalents found and the potential at the equivalence point, as well as a menu which provides the user with several choices (plotting the first and second derivatives, scaling up or down, etc.).

We also carried out an experiment using an Ag wire as indicator electrode, but the results yielded anomalously large errors which were attributed to the gradual build-up of an AgCl layer on the Ag wire indicator electrode that was rather difficult to remove by automatic washings between samples and, thus, resulted in spurious results. As a result, while the Ag wire and the chloride-selective electrode yielded similar results in the first few analyses, the latter allowed a much greater number of samples to be assayed reliably and was thus chosen for further experiments.

Table 1 lists the reproducibility achieved and the errors calculated after applying

Table 1 Reproducibility (%RSD) obtained and error found (%E) at different Ag generation intensities and Cl$^-$ contents ($n=4$)

Cl$^-$ content (μeq)	*i(mA)*	*Cl$^-$ found(μeq)*	*E(%)*	*RSD(%)*
4	5	4.13	3.3	1.9
4	10	3.86	−3.4	3.3
4	15	4.12	3.1	3.7
10	5	9.83	−1.7	1.7
10	10	10.02	0.2	0.9
10	15	9.91	−0.9	1.2
20	5	19.94	−0.3	0.3
20	10	20.14	0.7	0.6
20	15	20.22	1.1	0.8
40	5	39.88	−0.3	0.4
40	10	40.28	0.7	0.5
40	15	40.16	0.4	0.3

Table 2 Results obtained by applying the present and the Mohr method to the analysis of chloride in various types of water ($n=4$)

Water sample	*Chloride found (ppm)*				*Per cent difference*
	Mohr method	*%RSD*	*Coulom. method*	*%RSD*	
Waste 1	343	0.3	332	0.7	−3.2
Waste 2	346	0.4	343	0.1	−1.1
Waste 3	352	1.1	338	1.9	−3.9
Waste 4	349	0.7	336	0.2	−3.9
Tap 1	1019	0.6	1042	0.5	2.3
Tap 2	66.3	1.7	64.5	1.0	−2.7
Tap 3	1473	0.5	1449	0.7	−1.6
Tap 4	75.5	1.6	74.4	1.4	−1.4
Tank	22.3	2.1	22.6	1.6	1.1
Well	57.2	1.2	56.1	1.4	−1.9
Mineral	21.3	1.1	20.3	1.7	−4.5

the above-mentioned correction at different current intensities for Ag generation and Cl$^-$ concentrations; the results were calculated from the data given in Figure 2. As can be seen from the table, the reproducibility was virtually independent of the current intensity throughout the range studied, though it did depend on the analyte concentration—it was considerably better at high analyte concentrations, as is to be expected.

Application

The proposed system was applied to the determination of chloride in waters from various sources. The accuracy of the results obtained was checked by comparing them with those provided by the Mohr method; both sets of results are listed in Table 2. As can be seen from the table, the mutual agreement of the data of the proposed and the Mohr method is good. The results obtained for the waste water samples indicate that no appreciable matrix effect occurs for the proposed method.

CONCLUSIONS

The proposed system and software are effectively applicable to the determination of chloride ion in waters from different sources. The system features the typical advantages of coulometric titrations (e.g. no need for standards); in addition, its automated operation allows a large number of analyses to be carried out unattendly (up to 13 samples can be assayed in a single run at a rate of about 5 min per sample), which permits each sample to be analysed repeatedly. This creates a problem with most other methods, particularly when a large number of samples is involved where the difficulty in preserving samples requires determinations to be performed as expeditiously as possible. The proposed system surpasses the Mohr method with regard to detection limits (about 3 mg of chloride ion for the Mohr method as against 0.2 mg for the proposed method) and in the possibility of assaying coloured samples (e.g. some waste waters) where indicator colour changes are rather difficult to detect.

Acknowledgement

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