

High-sensitive electrochemical indication of the end point of titration

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A new high-sensitive electrochemical method for determining the end point of titration has been developed. By using a new kind of pulse polarization of the indication electrode and an indication method for a chosen potential, a considerable improvement of the analytical signal can be achieved while not only the faradaic component of the indication current but also the nonfaradaic component is utilized. The new method, called "Switching potentiostatic amperometry" (SPA) makes possible to indicate the end point of titration with extremely high sensitivity. The model coulometric titrations of As(III) and Cr(VI) in concentrations 10^{-6} — 10^{-9} mol dm⁻³ are presented as examples. The sensitivity of indication defined as the least substance amount in the titrated volume which produces an unambiguous signal in the course of transition through the end point is equal to 10^{-11} mol (in the volume 80 cm³) for the SPA method.

Разработан новый высокочувствительный электрохимический метод определения конца титрования. С помощью нового способа пульсной поляризации индикаторного электрода и с использованием метода индикации по выбранному потенциалу достигнуто значительное повышение аналитического сигнала, причем используется не только фарадеева составляющая индикаторного тока, но и нефарадеева составляющая. Новый метод, названный «Соединительная потенциостатическая амперометрия» (СПА), позволяет устанавливать конец титрования с исключительно высокой чувствительностью. В качестве примера приводятся модельные кулонометрические титрования As(III) и Cr(VI) с концентрациями от 10^{-6} до 10^{-9} моль дм⁻³. Чувствительность индикации, определяемая как минимальное количество вещества, которое в титруемом объеме вызывает появление однозначного сигнала при переходе через конец титрования, в методе СПА составляет 10^{-11} моль (в объеме 80 см³).

The magnitude of analytical signal in titration and thus the slope of titration curve as well as the concentration limit of titrability depends on the method of

indication of the end point of titration. We may say that the determination of the end point represents one of the main problems of the trace titration analysis. In most titration methods the concentration limit of determination varies within the range 10^{-4} — 10^{-6} mol dm $^{-3}$. The electrochemical voltammetric indication methods are characterized by high sensitivity. Among potentiometric methods, it is namely the direct current and alternating current differential electrolytic potentiometry [1] which utilizes the activation overpotential. The methods with amperometric and biamperometric indication are most frequently used for coulometric titrations. From the view-point of the aspects of trace analysis, these methods may be divided into two groups. The first group comprises the methods employing electrodes with large surface or forced convection where relatively high indication currents are attained. The biamperometric and amperometric titrations with rotating disc electrode or mercury electrode with large surface area may serve as examples. Of course, high indication currents can change concentration of the determined components owing to electrolysis. This problem can be solved by such connection of the indication and generation circuit that the indication current may serve as a component of the generation current of coulometric titration [2]. The second group is represented by the methods of alternating, pulse, and differential pulse voltammetry which are characterized by high sensitivity [3, 4].

Cooke, Reilley, and Furman [5] elaborated a simple and sensitive amperometric method of titration to a chosen potential. This end potential is chosen in the steepest part of the potentiometric titration curve and imposed upon the indication electrode by a proper direct voltage supply. The attainment of this potential is followed by means of an amperometric circuit during the titration. The method was applied to determination of the iron(II) ions by the coulometrically generated cerium(IV) ions on the concentration level 10^{-7} mol dm $^{-3}$. *Champion, Marinenko, Taylor, and Schmidt* [6] used amperometric indication for determining chromium by coulometric titration on the concentration level 0.5×10^{-7} mol dm $^{-3}$. The success of the method was due to construction of a small titration cell and improvement of amperometric detection system. The amperometric titrations using the differential and normal pulse polarography were carried out by *Osteryoung et al.* [3, 4] on the concentration level 10^{-7} mol dm $^{-3}$. The merit of these techniques consists in reduction of the contribution of capacity current in the analytical signal when compared with other polarographic methods. However, a part of the capacity current remains, impairs the ratio of analytical signal to noise and represents the limiting factor of these methods in trace titration analysis.

In general, the ratio of analytical signal to disturbing signals is unfavourable in the region of low concentrations and the indication of concentration change becomes difficult. Further advancement of the limit of determination may be

achieved only by raising this ratio, which is possible either by improving the sensitivity of indication (the value of analytical signal corresponding to a certain concentration change or the least substance amount which produces an unambiguous signal at the end point in the titrated volume) or by reducing the influence of disturbing signals.

The new high-sensitive electrochemical method of determination of the end point of titration [7—9] employs both possible ways for improving the ratio of signal to noise and advancing the limit of determination towards lower concentrations. By means of a new kind of the pulse polarization of indication electrode and using the method of indication to a chosen potential [5] we achieved a significant elevation of analytical signal. In contrast to all hitherto used electrochemical methods of indication, not only the faradaic component of indication current but also the nonfaradaic component, *i. e.* the capacity current is employed as analytical signal. The capacity current represents the noise component in other amperometric indication methods and is a limiting factor for improvement of their sensitivity. The new method called "Switching potentiostatic amperometry" (SPA) makes possible to indicate the end point of titration with extremely high sensitivity.

Experimental

Chemicals and solutions

The experiments were performed with anal. grade chemicals (H_2SO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, KI, KCl, As_2O_3 , NaOH, H_2O_2) and argon for electric bulb industry. Fresh redistilled water was used for preparation of solutions.

The solutions of $\text{K}_2\text{Cr}_2\text{O}_7$ ($c(1/6\text{K}_2\text{Cr}_2\text{O}_7) = 1 \times 10^{-2} \text{ mol dm}^{-3}$) and sodium arsenite ($c(\text{As}(\text{III})) = 5 \times 10^{-2} \text{ mol dm}^{-3}$) were used as standard solutions. The solution of sodium arsenite was prepared by dissolving the weighed amount of As_2O_3 in 10 % solution of NaOH in the absence of air oxygen and filling up to the mark with phosphate buffer solution. These solutions were used for preparing solutions of lower concentration by diluting.

The solutions of $\text{NH}_4\text{Fe}(\text{III})\text{SO}_4$ ($c(\text{Fe}(\text{III})) = 0.4 \text{ mol dm}^{-3}$) and H_2SO_4 ($c(\text{H}_2\text{SO}_4) = 2 \text{ mol dm}^{-3}$) were used as ground electrolytes in function of auxiliary systems for coulometric titrations. The solution of $\text{NH}_4\text{Fe}(\text{SO}_4)_2$ was prepared by dissolving the anal. grade chemical in sulfuric acid (volume ratio $\varphi' = 1 : 1$) and filling up with water or by dissolving ammonium iron(II) sulfate in dilute sulfuric acid ($\varphi' = 1 : 1$) and oxidizing it with hydrogen peroxide at increased temperature. The excess peroxide was removed by boiling and catalytic action of a platinized platinum electrode. After cooling the solution was filled up to required concentration with water. The concentrations of KI,

Na_2HPO_4 , and KH_2PO_4 solutions were $c(\text{KI}) = 0.1 \text{ mol dm}^{-3}$, $c(\text{Na}_2\text{HPO}_4) = 0.1 \text{ mol dm}^{-3}$, and $c(\text{KH}_2\text{PO}_4) = 0.1 \text{ mol dm}^{-3}$ ($\text{pH} = 7.0$).

Instruments and equipments

For indicating the end point by the SPA method, the modular units VD600 SPA and VD600 SH were developed in the VD600 system (Department of Analytical Chemistry, Slovak Technical University, Bratislava). A polarograph OH-104 (Radelkis, Budapest) was used as recorder. The VD system was controlled by a microcomputer TEMS 8003A (Tesla, CSSR).

The measuring cell consisted of a titration vessel (Metrohm, type EA-875-50) and electrodes. The volume of electrolyte for one experiment was usually 80 cm^3 . All electrodes and argon supply were led through five ground holes in a closing cover of the vessel. The auxiliary platinum electrode of the indication and generation circuit and reference electrode (1 M-Ag/AgCl electrode or saturated calomel electrode) were isolated from solution by a glass bridge filled with H_2SO_4 of 2 mol dm^{-3} concentration. In some cases, a cell with nonseparated electrodes and a platinum microelectrode was used. The platinum electrodes of the form of wire or sheet were applied as indication or generation electrodes.

The solution was stirred with a magnetic stirrer.

For measuring samples and standard additions, piston feeders and microfeeders with polypropylene tips (Hamilton, Gilson) were used.

The coulometric measurements were carried out by means of a coulometer of the OH-404 type (Radelkis, Budapest).

Method

The block diagram of the indication circuit is represented in Fig. 1. The three-electrode measuring cell comprises indication electrode I, reference electrode R, and auxiliary electrode A. A periodically working switch S is connected in the circuit of indication

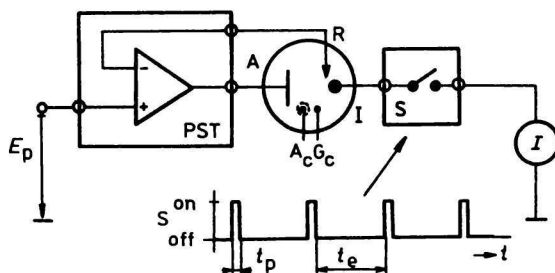
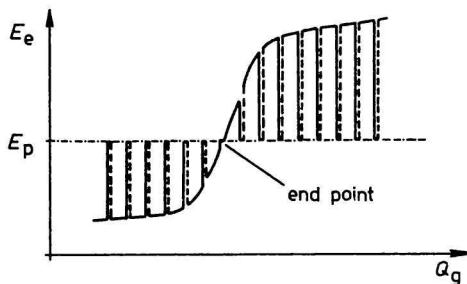


Fig. 1. Block diagram of the circuit for switching potentiostatic amperometry (PST — potentiostat, S — switch, I — indication electrode, R — reference electrode, A — auxiliary electrode, G_c — coulometric generation electrode, A_c — coulometric auxiliary electrode).

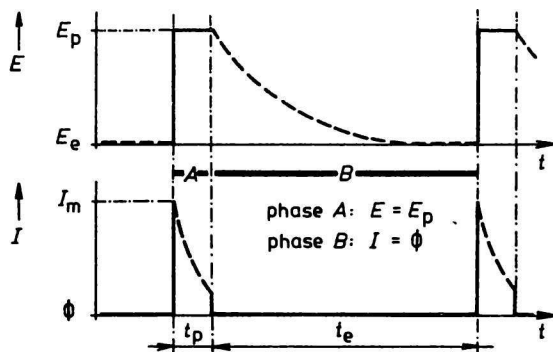
electrode. Owing to this fact, the indication electrode is polarized by potential pulses the amplitude of which is determined by equilibrium potential E_e (S is "off") and forced potential E_p (S is "on"). The time course of switching is represented in the lower part of Fig. 1. The overall current response of the indication electrode (superposition of faradaic and nonfaradaic component of current) is followed in the course of titration while the end point of titration is indicated by the change of polarity of the current response.

Fig. 2. Relationship between the pulse amplitude of polarization potential E_p and potentiometric titration curve of the determined component.



The equilibrium potential E_e , *i.e.* the potential at zero current is determined by the composition of electrolyte (for a given indication electrode). During the titration the value of E_e changes in conformity with the potentiometric titration curve. The forced potential E_p represents the end potential to which we titrate. The time response of the potential of indication electrode after disconnection of the polarization circuit by the switch S is like in chronopotentiometry (current pulse $I = 0$) and the equilibrium value of this potential is determined by the time of period, *i.e.* practically t_e and by the efficiency of stirring. The relationship between amplitude of a pulse and potentiometric titration curve is represented in Fig. 2. The courses of polarization pulse and current response are outlined in Fig. 3. It follows from Fig. 3 that the polarization pulses can be characterized by two stages. In the first stage the potential E_p is forced upon the indication electrode by potentiostat while the zero current is forced upon the indication electrode in the second stage. The determination of the end point of titration is made possible by the fact that the polarity of the faradaic as well as nonfaradaic component of the current response

Fig. 3. Time course of potential pulse and current response of the indication electrode.



of indication electrode changes when passing from inequality $E_p > E_e$ to inequality $E_p < E_e$. It is obvious that the current response must be equal to zero if the values of equilibrium and forced potential are equal, which indicates that the equilibrium potential has reached the value of the chosen end potential to which we are titrating. For other values of E_e , the current cannot equal zero and its polarity is determined by the polarity of E_e with respect to the forced potential E_p . Therefore we must titrate till the change of polarity of the current response of indication electrode appears.

Results and discussion

The current response of indication electrode corresponding to the potential pulse $E_p - E_e$ in the SPA method represents the sum of the faradaic and nonfaradaic component. The values of these components reach the maxima at the time $t \rightarrow 0$ and rapidly decrease with time to the values corresponding to D.C. hydrodynamic amperometry which are much lower. In order to obtain the possibly highest indication signal, we must therefore measure the current in the first moment of polarization pulse, *e.g.* by means of an electronic sampling circuit [10]. However, good results were also obtained by a simpler solution, *i.e.* by direct recording with sufficiently fast line recorder. The course of titrations using the SPA method as represented in Fig. 8 was recorded in this way. A polarograph OH-105 completed with a switching unit VD600 SPA which was connected in series with the indication electrode was used as recorder [9]. It has been disclosed that this solution shows some merits in spite of a poorer utilization of the sensitivity of the SPA method. The signal is of dynamic character with return to the zero line, which facilitates indication of the end point in manual performance of the titration. It is not necessary to alter sensitivity of the recorder during titration. The maximum sensitivity of the mentioned type of recorder is to be adjusted at the beginning of measurement. The strong signal at the start of titration was automatically impaired by the maximum velocity of the run of pen of the recorder.

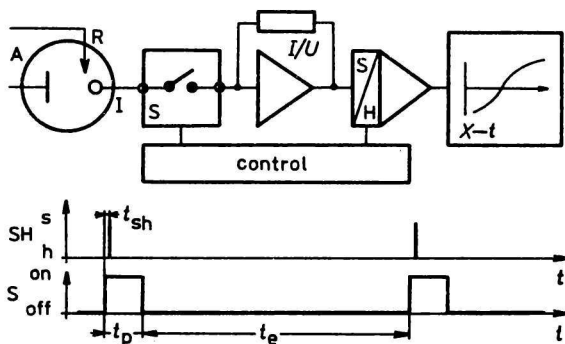


Fig. 4. Block diagram of the circuit for switching potentiostatic amperometry with sampling.

The indication unit VD600 SH [9] has been developed for further enhancement of sensitivity of indication and study of the SPA method. Its block diagram is outlined in Fig. 4. The activity of this unit is controlled by a microcomputer according to the scheme in the lower part of Fig. 4.

By means of the modul unit VD600 SM the $I-t$ curves were taken for solutions where the coulometric titrations were carried out. The aim of this study has not been to analyze in more detail the course and proportion of individual components of the indication current. It is known that the charging component of current decreases exponentially with time and becomes negligible at time exceeding the product of the capacity of electric double layer and resistance of electrolyte, while the faradaic component decreases with square root of time, *i.e.* slower. For short times which are comparable with the transport time through the diffusion layer in a stirred solution, the faradaic transition current shall exhibit equal character as observed in the case of potential change in a nonstirred solution (the width of the Nernst layer is much greater than the width of the diffusion layer during short pulse). These problems are more deeply analyzed in papers [11–13]. Fig. 5 gives the courses of $I(t)$ and $I(\sqrt{t})$ which were measured in a solution containing the component Cr(VI) ($c(\text{Cr(VI)}) = 2 \times 10^{-4} \text{ mol dm}^{-3}$) at $E_p = +0.750 \text{ V}$ (*vs.* a 1 M-Ag/AgCl electrode).

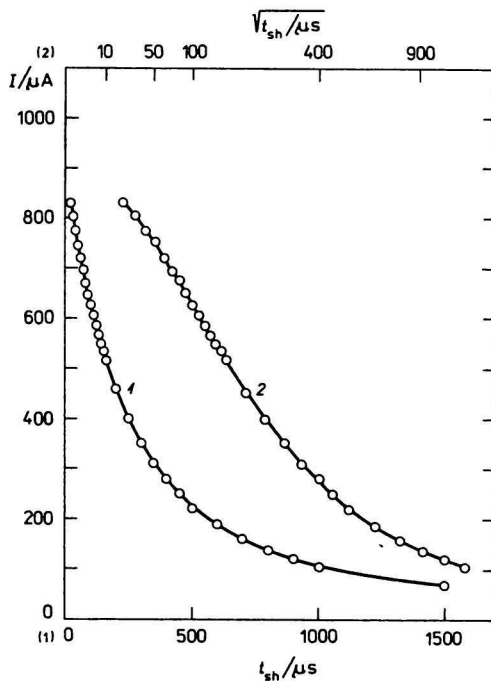


Fig. 5. Experimental time course of the indication current.

1. $I(t)$ curve; 2. $I(\sqrt{t})$ curve.

Curve 1 describes the dependence of the instantaneous value of indication current on the sampling time t_{sh} which varied from $20\mu\text{s}$ to 20ms . Curve 2 represents the dependence of the instantaneous value of indication current on the square root of the sampling time t_{sh} . The character of the dependence for $t_{sh} < 40\mu\text{s}$ may be affected by experimental equipment while the course for $t_{sh} > 2.5\text{ms}$ is consistent with discussion in paper [11] or [12]. Fig. 5 also gives information about improvement of the sensitivity of the SPA method when compared with D.C. amperometric indication.

The high sensitivity of the SPA method is also reflected in the course of the polarization curves recorded at different sampling times t_{sh} . The polarization curves obtained for potassium dichromate are presented in Fig. 6. Curve 9 was measured by using the D.C. method. It appears that the value of the D.C. signal is very small in comparison with the SPA signal if the reaction is carried out for instance at the potential $E_p = +0.750\text{V}$ where the reduction of dichromate

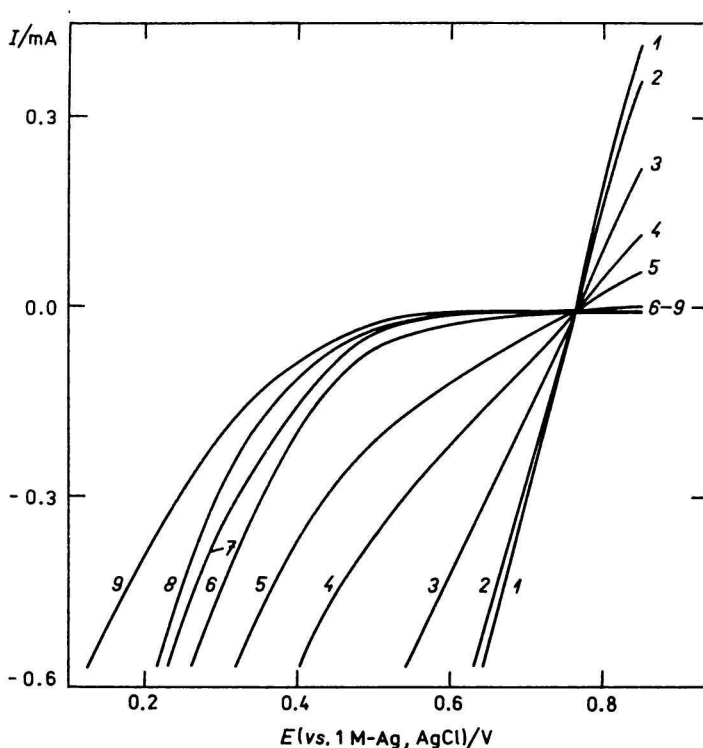


Fig. 6. Polarization curves (1—8) recorded by the use of the SPA method at sampling times $t_{sh} = 20\mu\text{s}$ — 100ms in solutions of $\text{K}_2\text{Cr}_2\text{O}_7$ ($c(1/6\text{K}_2\text{Cr}_2\text{O}_7) \approx 5.4 \times 10^{-3}\text{mol dm}^{-3}$), $\text{NH}_4\text{Fe}(\text{SO}_4)_2$ ($c(\text{NH}_4\text{Fe}(\text{SO}_4)_2) = 0.4\text{mol dm}^{-3}$), and H_2SO_4 ($c(\text{H}_2\text{SO}_4) = 2\text{mol dm}^{-3}$) ($t_c = 2\text{s}$, $t_p = 200\text{ms}$). Curve 9 recorded by the use of the D.C. method, scan = 0.1V min^{-1} .

starts to be operative. Analogous conclusion may be also drawn from Fig. 7 which represents the polarization curves for a solution of the Fe(II) and Fe(III) ions. The oxidation of Fe(II) shall take place at the potential of + 0.750 V and the strength of the SPA signal may be much higher when compared with the signal obtained by the D.C. method.

A typical course of coulometric SPA titration curve directly recorded by a polarograph OH-105 with a unit VD600 SPA, *i.e.* without electronic sampling of signal is outlined in Fig. 8. It refers to the titration of 80 cm³ of As(III)

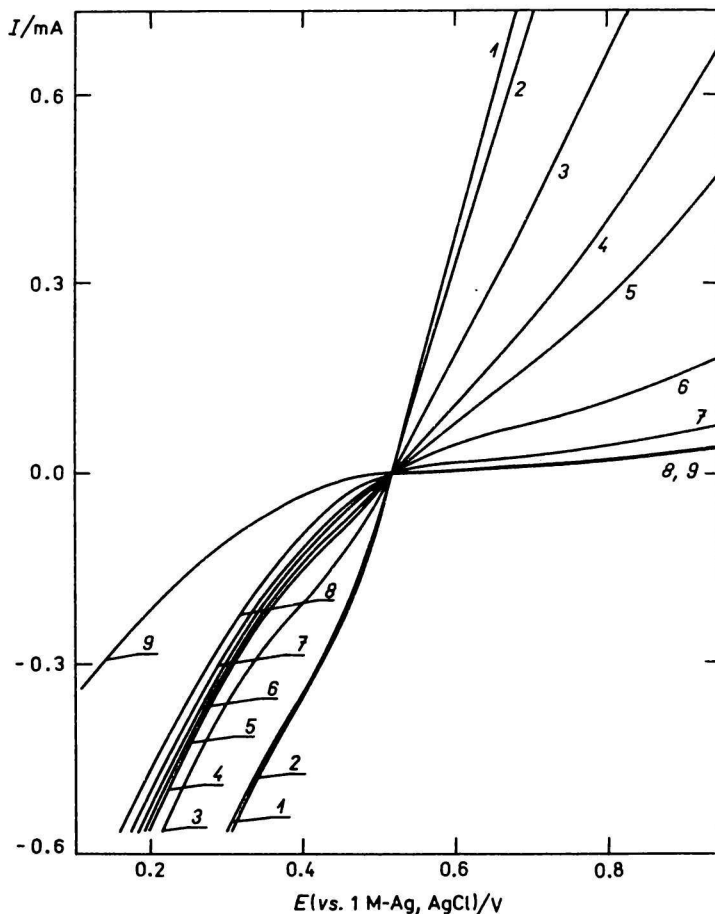


Fig. 7. Polarization curves (1-8) recorded by the use of the SPA method at sampling times $t_{sh} = 20 \mu s-100 ms$ in solutions of Fe(III) ($c(\text{Fe(III)}) = 0.4 \text{ mol dm}^{-3}$), Fe(II) ($c(\text{Fe(II)}) = 8 \times 10^{-4} \text{ mol dm}^{-3}$), and H_2SO_4 ($c(\text{H}_2\text{SO}_4) = 2 \text{ mol dm}^{-3}$) ($t_c = 2 s$, $t_p = 200 ms$). Curve 9 recorded by the use of the D.C. method, scan = 0.1 V min^{-1} .

solution ($c(\text{As(III)}) = 6.25 \times 10^{-8} \text{ mol dm}^{-3}$) by iodine generated by the current of $4.4 \mu\text{A}$. The coulometric titration SPA curve recorded with the sampling of signal is represented in Fig. 9. The titration of 80 cm^3 of the potassium dichromate solution ($c(1/6\text{K}_2\text{Cr}_2\text{O}_7) = 2 \times 10^{-5} \text{ mol dm}^{-3}$) was performed with the generated Fe(II) ions. In the course of titration the generation current was manually changed from 1.00 mA to $5.00 \mu\text{A}$. The end point of titration is represented by the intersection of the curve with the zero axis.

A survey of the results of coulometric titrations of As(III) and Cr(VI) obtained by the use of SPA indication is presented in Table 1. The results of a

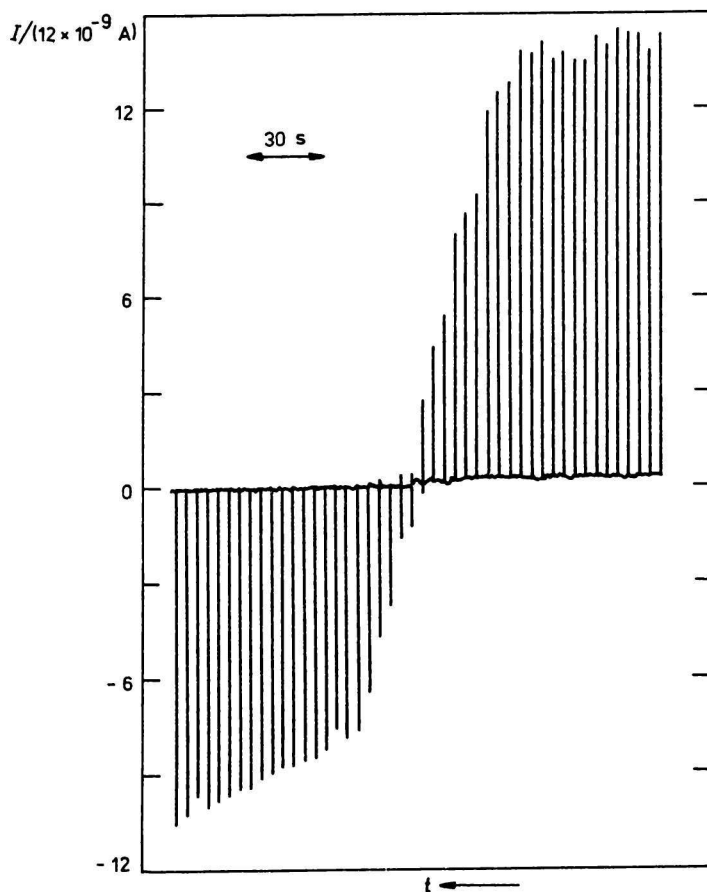
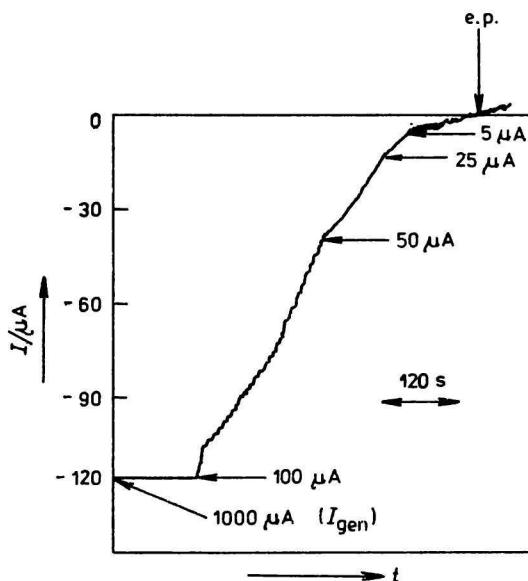


Fig. 8. Coulometric titration curve of As(III) solution with SPA indication (80 cm^3 , $c(\text{As(III)}) = 6.25 \times 10^{-8} \text{ mol dm}^{-3}$ in the medium of KI ($c(\text{KI}) = 0.1 \text{ mol dm}^{-3}$), Na_2HPO_4 ($c(\text{Na}_2\text{HPO}_4) = 0.1 \text{ mol dm}^{-3}$), and KH_2PO_4 ($c(\text{KH}_2\text{PO}_4) = 0.1 \text{ mol dm}^{-3}$)); $I_{\text{gen}} = 4.4 \mu\text{A}$; $E_p = 0.215 \text{ V}$ (vs. 1 M-Ag/AgCl); $t_e = 2 \text{ s}$; $t_p = 200 \text{ ms}$).

Fig. 9. Coulometric titration curve of Cr(VI) solution with SPA indication (80 cm^3 , $c(1/6\text{K}_2\text{Cr}_2\text{O}_7) = 2 \times 10^{-5} \text{ mol dm}^{-3}$ in the medium of Fe(III) ($c(\text{Fe(III)}) = 0.4 \text{ mol dm}^{-3}$) and H_2SO_4 ($c(\text{H}_2\text{SO}_4) = 2 \text{ mol dm}^{-3}$)); in the course of titration the generation current was manually adjusted from 1.00 mA to $5 \mu\text{A}$; $t_e = 5 \text{ s}$; $t_p = 10 \text{ ms}$; $t_{sh} = 0.2 \text{ ms}$; $E_p = 0.750 \text{ V}$ (vs. 1 M-Ag/AgCl).



great number of titrations of model solutions with concentrations $10^{-6} \text{ mol dm}^{-3}$ — $10^{-9} \text{ mol dm}^{-3}$ were processed by linear regression. The coefficients of correlation varied within the range 0.9990 — 0.9999 . In most cases, the regression lines went through the origin. The section on the concentration axis was not negligible only in the case of very low concentrations

Table 1

Summary list of the results of coulometric titrations of As(III) and Cr(VI) obtained by means of SPA indication

c — concentration range of the titrated solutions; n — substance amounts of the titrated components; s_r — relative standard deviation

	As(III)	Cr(VI)
$c/(\text{mol dm}^{-3})$	6.2×10^{-7} — 6.2×10^{-9}	1.7×10^{-6} — 4×10^{-9}
n/mol	5×10^{-8} — 5×10^{-10}	1.3×10^{-7} — 3.3×10^{-10}
$s_r/\%$	0.7—7	1.2—5
The limit of determination		
mol	1×10^{-10}	6×10^{-11}
Concentration limit of titration		
mol dm^{-3}	1.2×10^{-9}	8×10^{-10}
E_p (vs. 1 M-Ag/AgCl)/V	0.215	0.750

($c \approx 10^{-8} \text{ mol dm}^{-3}$). That is evidently in relation to the problems of positive or negative contamination which are the major problems in the trace analysis. As for the determination of arsenic and chromium, Table 1 shows that the method of SPA indication may be used for titration of the solutions of $1 \times 10^{-9} \text{ mol dm}^{-3}$ concentration, which represents the substance amount of $8 \times 10^{-11} \text{ mol dm}^{-3}$ present in the titrated volume of 80 cm^3 . The relative standard deviation of titrations varied within the range 1%—7%.

On the basis of the obtained results, we may state that the developed new method of SPA indication of the end point of titration shows much higher sensitivity when compared with other voltammetric indication methods. The sensitivity of indication (the least substance amount which produces an unambiguous signal at transition through the end point in the titrated volume) is equal to 10^{-11} mol for the SPA method, which corresponds to $1 \mu\text{C}$ for 80 cm^3 of the solution. Owing to a small width of the indication pulse t_p and relatively long time t_e when the indication circuit is disconnected, the error due to electrolysis by the indication current is negligibly small. The contribution given by the capacity current favourably affects the sensitivity of indication. From the electrochemical point of view, it seems that the polarization generated by pulses with the amplitude $E_p - E_e$ has favourable influence on history, character, and properties of the electrode surface. From the instrumental point of view, the SPA method is suited to automation and based on simple construction. Because of these facts, we may regard the coulometric titration with SPA indication as a simple, rapid, precise, and inexpensive instrumental method and class it with prospective methods of trace analysis.

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