

Potentiometric application of boron- and phosphorus-doped glassy carbon electrodes

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(Received 19 September, revised 5 December 2000)

A comparative study was carried out of the potentiometric application of boron- and phosphorus-doped and undoped glassy carbon samples prepared at the same heat treatment temperature (HTT 1000 °C). The electrochemical activities of the obtained electrode materials were investigated on the example of argentometric titrations. It was found that the electrochemical behaviour of the doped glassy carbon samples are very similar to a Sigrí (undoped) glassy carbon sample (HTT 2400 °C). The experiments showed that the potentiometric response depends on the polarization mode, the nature of the sample, the pretreatment of the electrode surface, and the nature of the supporting electrolyte. The amounts of iodide, bromide, and of chloride were determined to be 1.27 mg, 0.80 mg and 0.54 mg, respectively, with a maximum relative standard deviation of less than 1.1 %. The obtained results are in good agreement with the results of comparative potentiometric titrations using a silver indicator electrode. The titration method was applied to the indirect determination of pyridoxine hydrochloride, *i.e.*, vitamin B₆.

Keywords: boron- and phosphorus-doped glassy carbon electrodes; potentiometric titration of halides; determination of vitamin B₆.

INTRODUCTION

Recently, great attention has been paid to the study of the electrochemical properties of some new carbonaceous materials homogeneously modified, rather than surface modified.¹ Namely, it is to be expected that an electrode modified at the atomic level would exhibit efficient catalysis, high stability, and comparatively simple renewability. Glassy carbons (GC) involving a variety of heteroatoms, including nitrogen, silicon, and halide have been prepared by thermolysis of the appropriate precursors.^{1,2} A recent study³ showed that doping glassy carbon with boron and phosphorus significantly changed the surface properties of the material.

In our previous work, one of the research directions was the applicability of various carbonaceous electrodes for monitoring the course of amperometric and potentiometric ti-

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trations of different substances.⁴⁻¹² In continuation of these investigations, in the present work, the potentiometric application of boron- and phosphorus-doped and undoped glassy carbon electrodes, prepared at the same heat treatment temperature (HTT 1000 °C), for the determination of halides was studied. The developed procedure was also applied for the analysis of pyridoxine hydrochloride (4,5-dimethylol-3-hydroxy-2-methylpyridine hydrochloride, C₈H₁₁NO₃ HCl, relative molar mass $M_r = 205.69$), *i.e.*, vitamin B₆.

EXPERIMENTAL

Chemicals and solutions

All employed chemicals were of analytical reagent grade. Solutions were prepared in doubly distilled water. The standard solution of silver nitrate had a concentration of $1 \cdot 10^{-2}$ mol/dm³. The concentration of the halide solutions was $1 \cdot 10^{-3}$ mol/dm³. The supporting electrolytes tested were solutions of sulphuric, nitric, and perchloric acids, as well as potassium nitrate and sodium perchlorate of different concentrations.

Pyridoxine hydrochloride was analyzed in Bedoxin tablets (ICN Galenika, Belgrade, Yugoslavia). The content of the active component, according to the declaration, was 20 mg per tablet.

Apparatus

The comparative investigations encompassed a GC sample doped with boron (B-GC10), containing 0.6 % of boron (w/w in the starting resin), a GC sample doped with phosphorus (P-GC10), containing 1.0 % of phosphorus in the starting resin, and an undoped sample (GC10). All the GC samples, in the form of rods (3 mm), were prepared by carbonization at 1000 °C of a phenol-formaldehyde resin, with (H₃BO₃ or P₂O₅)³ or without the doping element. The results were also compared with those of a Sigrü (undoped) GC sample whose heat-treatment temperature was 2400 °C (GC24), and a silver electrode. In all the experiments, only the electrode disc area was exposed to the solution, except for the silver electrode which was in the form of a wire.

The established optimal pretreatment procedure of the electrodes GC10, B-GC10, and P-GC10 involved their polishing with alumina (Buehler LTD, micropolish, Linde A, 0.3 µm Alpha alumina) wetted with doubly distilled water, to a mirror finish (about 5 min). Afterwards the electrode was washed in an ultrasonic bath with distilled water to remove any residual polish. In the titration of iodide, the electrode was polished with alumina at the beginning of each series of measurements, of bromide after each five, and of chloride after each titration. In all cases the electrode was washed before each titration. However, if the solution contained a supporting electrolyte, it was necessary to polish the electrode before each titration, then it was negatively polarized against a saturated calomel electrode (SCE) in distilled water (whose conductivity can be ascribed to the ions leached out from the electrolytic bridge and introduced with the electrode), to pass a current of $-5 \mu\text{A}$ for 5 min. When using the GC24 electrode it was necessary to repeat the whole pretreatment procedure before each titration, irrespective of the nature of the halide to be titrated. It is interesting to note that an *in situ* pretreatment in the solution to be titrated gave no satisfactory results.

The microcomputer-aided^{13,14} potentiometric titrations were carried out either at zero current or at a controlled-current, with two of the above-mentioned indicator electrodes GC (+) GC (−) or with one indicator electrode (polarized either positively GC (+) SCE (−), or negatively GC (−) SCE (+) and coupled to a SCE *via* a double-junction salt bridge. A current of $1 \mu\text{A}$ was chosen for the titration of iodide and bromide, and $2 \mu\text{A}$ for chloride. The titrant was added continuously using a Radiometer ABU 80 automatic piston burette at an optimum rate of 0.25 cm³/min.

Procedure

Four Bedoxin tablets were dissolved in water and diluted to volume in a 200 cm³ volumetric flask. Aliquots of 10.00 cm³ were used for titration.

The titration endpoint was determined using a computer program for finding the intersection of the straight lines before and after the equivalence point (iodide and bromide) or from the first derivative maximum (chloride). The results of the chloride determination were corrected for the blank.

RESULTS AND DISCUSSION

The objective of this work was a comparative study of the potentiometric application of boron- and phosphorus-doped and undoped glassy carbon samples prepared at 1000 °C in the argentometric titrations of halides, employing either zero-current or controlled-current potentiometric indication. The results were compared with those obtained using a GC24 and a silver wire electrode.

Optimization of conditions

Optimization experiments were carried out to find the best experimental conditions for the potentiometric titrations with respect to the polarization mode, the nature of the GC sample, the electrode pretreatment mode, and the nature of the supporting electrolyte.

Choice of method

The controlled-current potentiometric titration curves obtained with one P-GC10 indicator electrode polarized either positively (curve 1) or negatively (curve 3) both vs. SCE, as well as with two P-GC10 indicator electrodes (curve 4) are presented in Fig. 1. In the

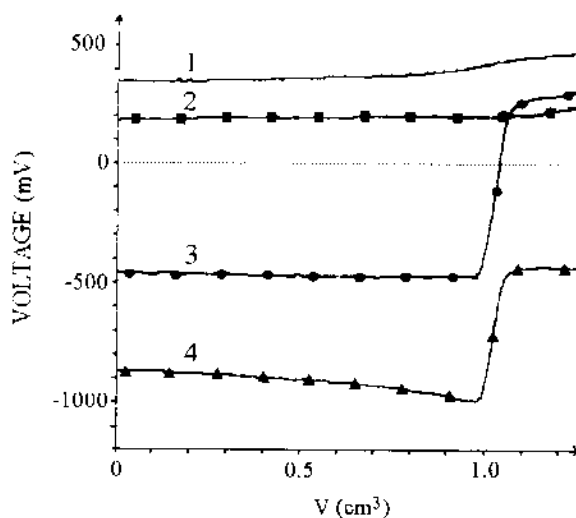


Fig. 1. Effect of the electrode polarization mode on the shape of the potentiometric titration curves of 1.27 mg iodide with $1 \cdot 10^{-2} \text{ mol/dm}^3 \text{ AgNO}_3$: 1) P-GC10(+) SCE(-), ($I = 1 \text{ A}$); 2) P-GC10 SCE, ($I = 0$); 3) P-GC10(-) SCE(+), ($I = 1 \text{ A}$); 4) P-GC10(+) P-GC10(-), ($I = 1 \text{ A}$).

same Figure the potentiometric titration curve at zero current (curve 2) is also shown. As can be seen, the best result was obtained with the negatively polarized indicator electrode. Experiments concerned with the optimal polarization mode of the other GC materials yielded the same conclusion. Therefore, this polarization mode was chosen in the further optimization experiments. The appropriate current intensity was chosen as the smallest one giving titration curves of satisfactory shape and reproducibility, and this was -1 A for the iodide and bromide titrations. However, the determination of chloride at this current resulted in poor reproducibility of the titration curves, which was significantly improved at -2 A .

Choice of indicator electrode

The effect of the nature of the GC sample on the shape of the titration curve is illustrated in Fig. 2. As can be seen, the glassy carbon doped with boron (curve 3) and

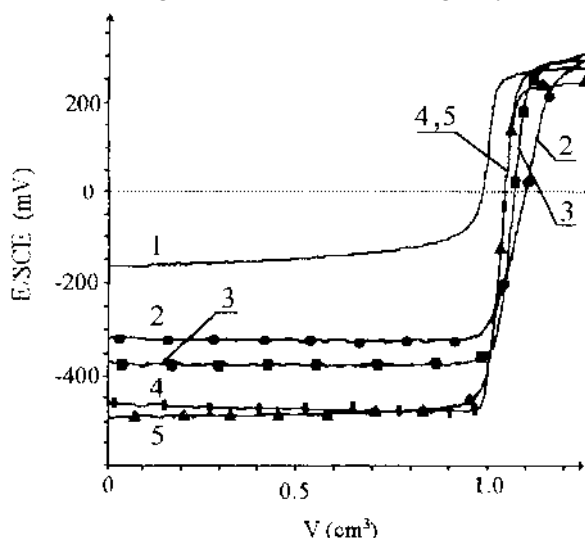


Fig. 2. Effect of the nature of the negatively polarized indicator electrode ($I = 1$ A) on the shape of the potentiometric titration curves of 1.27 mg of iodide with $1 \cdot 10^{-2}$ mol/dm³ AgNO₃: 1) Ag, ($I = 0$); 2) GC10; 3) B-GC10; 4) P-GC10; 5) GC24.

with phosphorus (curve 4) compared favourably with the undoped material (curve 2). However, all the mentioned glassy carbon electrodes (curves 2 – 4) are suitable for the determination of iodide, whereby the change of the potential around the equivalence point is in all cases greater than that obtained using a silver electrode (curve 1). Namely, before the titration end point, the potential is determined by the composition of the titration solution and after that by silver ions. Because of this, the electrode potential and the shape of the titration curve after the titration end point are very similar to those obtained with the Ag electrode. It can also be noticed that the inflection point of the curve obtained with the silver electrode (curve 1), which corresponds to the titration end point, coincides with the beginning of the abrupt change of the potential on the titration curves 2 – 4 obtained with the other electrodes. Hence, the titration end point in the cases when GC electrodes are used should be determined by extrapolating the straight portions of the titration curve before and after the equivalence point. However, in the titration of chloride, the shape of this part of the titration curve was not reproducible, so that the end point was determined from the first derivative maximum. Also, to obtain correct results, it was necessary to take into account the blank titration. By comparing the behaviour of GC24 (curve 5) with that of other glassy carbon electrodes (curves 2 – 4) it can be noticed that the total change of the potential is similar to that obtained with the P-GC10 electrode. The advantage of using the P-GC10 electrode compared with the B-GC10 and GC10 as indicator electrode is more obvious (not so much in the shape of the curve as in the precision of the determination) in the determination of bromides, and especially of chlorides.

Effect of supporting electrolyte

Effect of acids. Sulphuric, nitric, and perchloric acids were tested. The effect of the concentration of sulphuric acid as supporting electrolyte on the shape of the obtained titration curves using the investigated B-GC10 electrode is illustrated in Fig. 3. It is evident that the most suitable titration curve is obtained in the absence of supporting electrolyte (curve 5). The presence of sulphuric acid in concentrations from $3.3 \cdot 10^{-3}$ to 1.3 mol/dm^3 (curves 2–4) resulted in changes of the shape of the titration curves: increasing the concentration lead to a decrease in the rate of the potential change after the end point, as well as in an increase of the initial potential. This resulted in a decrease of the potential jump around the titration end point, so that at a concentration of 0.33

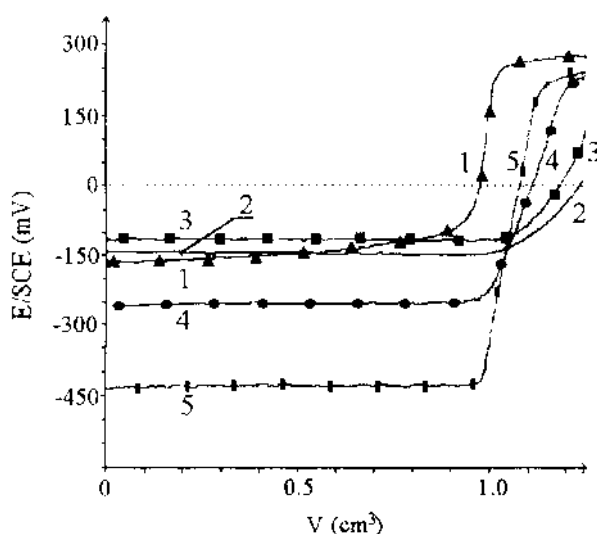


Fig. 3. Effect of H_2SO_4 concentration on the shape of the potentiometric B-GC10(-) SCE(+) ($I=1 \text{ A}$) titration curves of 1.27 mg of iodide with $1 \cdot 10^{-2} \text{ mol/dm}^3 \text{ AgNO}_3$: 1) Ag, ($I=0$) in the absence of H_2SO_4 ; 2) $1.3 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$; 3) $0.33 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$; 4) $3.3 \cdot 10^{-3} \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$; 5) in the absence of H_2SO_4 .

mol/dm^3 , and higher, the determination of iodide was hindered. With the P-GC10 electrode, the effect of H_2SO_4 concentration was also remarkable: at $3.3 \cdot 10^{-3} \text{ mol/dm}^3$ the electrode behaved more like a silver one, while at higher concentrations the curves have a similar shape as in the absence of H_2SO_4 , but with a smaller potential jump. The effect is least pronounced with the GC10 electrode. Finally, for the sake of comparison, the same effect was investigated using the GC24 electrode. In this case too, the presence of sulphuric acid had a significant effect, and at a concentration of 0.33 mol/dm^3 the electrode behaved more like a silver one. The more positive initial potential is a consequence of the reaction of proton reduction on the glassy carbon electrodes. However, it would be desirable to have the most negative initial electrode potential possible, as this would ensure the greatest potential jump around the titration end point. A similar behaviour of the electrodes was also observed in the presence of nitric and perchloric acids, whereby in the solution of perchloric acid the initial potential was more positive, which is a consequence of hydrogen evolution being more efficient from this acid.

The effect of sulphuric acid on the shape of the titration curve of chloride using B-GC10 as the indicator electrode is illustrated in Fig. 4 (curves 2 and 4). As can be

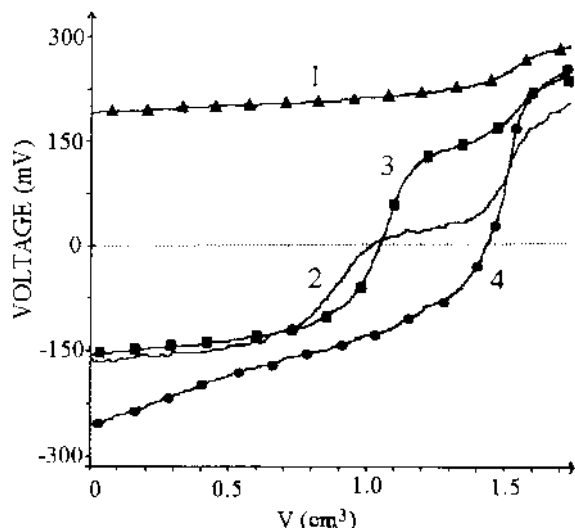


Fig. 4. Effect of the supporting electrolyte on the shape of the potentiometric [B-GC10(-) SCE ($I = 1$ A) titration curves of 0.54 mg of chloride with $1 \cdot 10^{-2}$ mol/dm³ AgNO₃: 1) Ag/SCE, ($I = 0$) in the absence of the supporting electrolyte; 2) 1.3 mol/dm³ H₂SO₄; 3) 0.25 mol/dm³ KNO₃; 4) in the absence of the supporting electrolyte.

seen, the presence of sulphuric acid resulted in a more positive initial potential, as well as in the appearance of another potential jump before the end point, hence the potential jump around the titration end point is lowered. Thus, in this case, the shape of the titration curves before the titration end point is also similar to the one obtained with silver electrode (Fig. 4, curve 1). The appearance of two potential jumps in the presence of acids is probably the consequence of the facilitated adsorption of the precipitate on the GC surface, which makes it behave as though it were a silver one. The difference in the potential of Ag electrode (curve 1) and that of the B-GC10 measured after the first potential jump (curve 2) is probably a consequence of the fact that curve 1 was obtained at $I = 0$ and curve 2 at $I = 1$ A. The same holds for the bromide titration. It appears that best reproducibility is obtained in the absence of acids (Fig. 4, curve 4).

Effect of salts. In studying the effect of potassium nitrate and sodium perchlorate (0.1 mol/dm³ or higher) as supporting electrolytes on the titration results, it was noticed that they did not significantly affect the initial electrode potential (Fig. 4, curves 3 and 4), but two potential jumps appeared irrespective of the nature of the titrated ion, *i.e.*, the GC electrodes also behave as a silver electrode before the end point (Fig. 4, curve 1). As with acidic solutions, the appearance of two potential jumps in the presence of salts is probably a consequence of the facilitated adsorption of the precipitate on the GC surface, thus making it behave as though it were a silver one. In an attempt to eliminate the appearance of two potential jumps, the effect of current intensity was investigated. It was found that at a current of -3 A the first jump was practically absent. This observation is also in agreement with the optimal pretreatment procedure of the GC electrodes when the solution contains a supporting electrolyte (see Apparatus). As the silver chloride precipitate is more readily adsorbed on the electrode surface than either silver bromide or iodide, this probably explains why is necessary to polish the GC electrodes after each chloride titration (even in the absence of supporting electrolyte), which is not the case with the bromide and iodide titrations. However, although intensive polishing of

the electrode ensured the removal of the precipitate from its surface, the electrode lost as a consequence some favourable properties it had attained due to negative polarization. Namely, negative polarization of the indicator electrode causes oxygen-containing surface groups to be reduced, which appears to be beneficial in argentometric titrations. Hence, after polishing, the electrode was polarized in distilled water containing a little potassium nitrate (about 10^{-5} mol/dm³), so that at a current of -5 A it acquired a relatively high negative potential (about -1.0 V vs. SCE).

The addition of a salt (*e.g.*, sodium carbonate) which causes an increase in the solution pH to 10, did not affect the shape of the titration curve.

Applicability of the method

Potentiometric titration curves for iodide, bromide, and chloride obtained with the aid of the P-GC10 electrode and the silver wire are presented in Figs. 5 and 6, respectively. It is evident that the potential jumps around the equivalence points are much larger in the case of the P-GC10 electrode, which ensure a more precise determination of the ions. Besides, these potential jumps are also dependent on the nature of the halide titrated. All this confirms the known observations that subtle differences in the electrode material can result in their different responses.

The results of the halide determinations are given in Table I. The maximum relative standard deviation (RSD) is 1.1 %. The results of the controlled-current potentiometric determination of iodide and bromide are in good agreement with those obtained using the silver wire. However, the shapes of the curves obtained in the titration of chloride using the GC10 indicator electrode were irreproducible (RSD 4.4%), so that this electrode was not applicable for this determination. The results obtained using the other four electrodes differed significantly in respect of the accuracy (one-factor analysis of variance, *F*-distribution). Only when the Sigris electrode was used were significant differences between the taken and found amounts of chloride obtained (Table I).

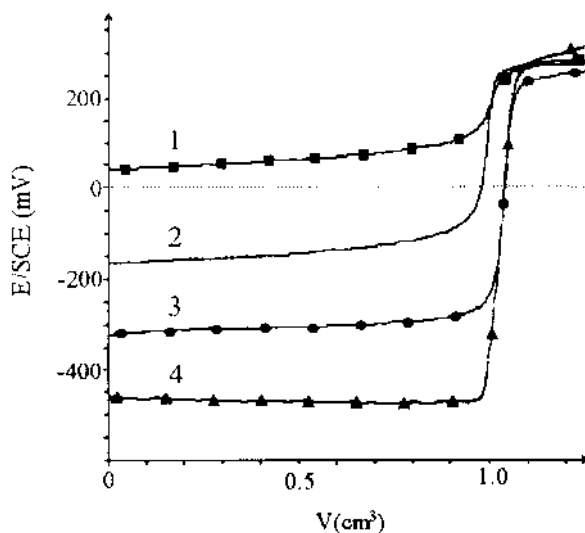


Fig. 5. Potentiometric titration curves of 0.80 mg of bromide (1, 3) and 1.27 mg of iodide (2, 4) with $1 \cdot 10^{-2}$ mol/dm³ AgNO₃: 1) and 2) Ag, (*I* = 0); 3) and 4) P-GC10(-) SCE(+), (*I* = 1)

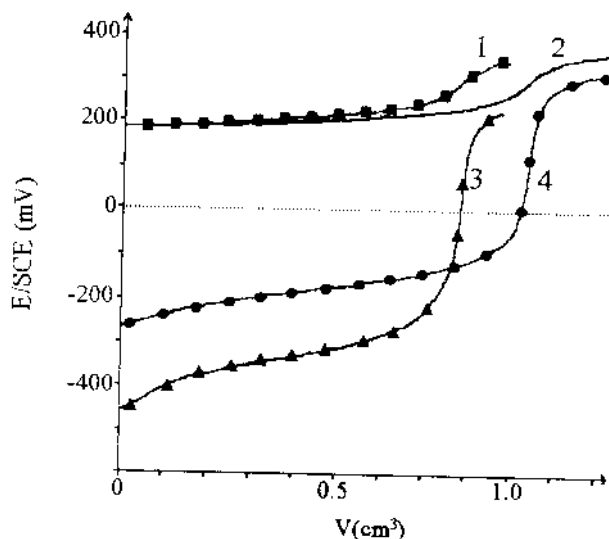


Fig. 6. Potentiometric titration curves of 0.54 mg of chloride (1, 3) and 4.0 mg of pyridoxine hydrochloride (2, 4) with $1 \cdot 10^{-2} \text{ mol/dm}^3 \text{ AgNO}_3$: 1) and 2) Ag, ($I=0$); 3) and 4) P-GC10(-) SCE(+), ($I=2 \text{ A}$).

The application of GC electrodes enables the titration of even ten times smaller amounts of iodide and bromide than those presented in Table I. It is interesting to note that, in contrast to the Ag-wire, the potential change after the equivalence point (in the absence of a higher concentration of the supporting electrolyte) is greater at lower halide concentrations, which increases the suitability of this method.

TABLE I. Results of argentometric potentiometric titrations of halides by application of various indicator electrodes ($n = 6$)

Method of endpoint determination		Titration substances						
		Iodide		Bromide		Chloride		<i>t</i> -test
		Found (mg) ¹	RSD (%)	Found (mg) ²	RSD (%)	Found (mg) ³	RSD (%)	
Controlled-current potentiometric titration	GC10	1.264	0.69	0.800	0.76	–	–	–
	B-GC10	1.266	0.27	0.808	0.64	0.538	1.08	0.15
	P-GC10	1.266	0.60	0.806	0.31	0.540	0.36	0.44
	GC24	1.259	0.68	0.801	0.87	0.523	0.83	3.21
Potentiometric (Ag/SCE) titration		1.265	0.50	0.801	0.64	0.553	1.76	1.25
F-test		1.09 ⁺		2.33 ⁺		24.07 [#]		

¹taken $\text{I}^- = 1.27 \text{ mg}$, ²taken $\text{Br}^- = 0.80 \text{ mg}$; ³taken $\text{Cl}^- = 0.54 \text{ mg}$. $t_{0.05;5} = 2.02$; $t_{0.01;5} = 3.36$; $^+F_{0.05;4,25} = 2.76$; $^{\#}F_{0.01;3,20} = 4.94$

Effect of foreign ions

Foreign ions that form precipitates with silver ions (carbonate, phosphate, sulphide) show the expected effect on the titration results. Namely, by adjusting the solu-

tion pH, the affect of the presence of these anions on the titration results can be eliminated. However, while carbonates and phosphates are not titrated, sulphides are selectively titrated, giving two inflexion points on the titration curve.

Titration of pyridoxine hydrochloride in Bedoxin tablets

Figure 6 shows the controlled-current potentiometric titration curves of pyridoxine hydrochloride (vitamin B₆) obtained with the P-GC10 (curve 4) and with the silver wire electrode (curve 2). In this case too, the advantage of the P-GC10 electrode is obvious. The results obtained using the P-GC10 electrode (19.90 mg, RSD 0.62) and the Ag-wire (19.80 mg, RSD 0.46) are in good agreement with the declared content of pyridoxine hydrochloride (20 mg per tablet). If our indirect method is compared with the approved method,¹⁵ there are substantial differences between them in respect to the sample preparation, *i.e.*, our method is simpler and faster. Our method is also advantageous in respect to the required amount of sample, *i.e.*, a 25 times smaller amount is required, and no special sample preparation procedure is needed.

CONCLUSION

Boron- and phosphorus-doped glassy carbon samples appear to be suitable electroanalytical sensors for monitoring the course of argentometric titrations. Depending on the experimental conditions, these electrodes are better than or equally good as a Ag-wire electrode.

Acknowledgement: This work was supported by the Ministry for Science and Technology of the Republic of Serbia.

ИЗВОД

ПРИМЕНА ЕЛЕКТРОДА ОД СТАКЛАСТОГ УГЉЕНИКА ДОПОВАНОГ БОРОМ И ФОСФОРОМ У ПОТЕНЦИОМЕТРИЈИ

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Испитана је могућност примене електрода од стакластог угљеника, како допованог бором и фосфором, тако и недопованог, као потенциометријског сензора. Сви узорци су припремљени при истој температури карбонизације (НТТ 1000 °С). Електрохемијска активност наведених електродних материјала је испитана на примеру аргентометријских титрација. Нађено је да су електрохемијске особине допованих узорака врло сличне недопованом стакластом угљенику производње Sigrі (НТТ 2400 °С). Експерименти показују да потенциометријски одговор зависи од начина поларизације, природе узорка, начина третирања електрода и природе основног електролита. Одређиване су количине од 1,27 mg јодида, 0,80 mg бромида и 0,54 mg хлорида са максималном релативном стандардном девијацијом мањом од 1,1 %. Постигнути резултати се добро слажу са резултатима упоредних потенциометријских титрација применом сребрне индикаторске електроде. Титрациона метода је примењена за индиректно одређивање пиридоксин хидрохлорида, тј. витамина В₆.

(Примљено 19. септембра, ревидирано 5. децембра 2000)

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