SCIENTIFIC PAPERS
OF THE UNIVERSITY OF PARDUBICE
Series A
Faculty of Chemical Technology
7 (2001)

CONSTRUCTION OF SOME NEW SIMPLE MALACHITE GREEN ION-SELECTIVE ELECTRODES

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Received August 27, 2001

The construction and performance characteristics of different types of malachite green ion–selective electrodes are described. These electrodes were prepared either by coating different substrates (metal wires, carbon rode, glass electrode, solid contact electrodes) or like conventional polymeric membrane electrodes with an electroactive material containing malachite green tetraphenylborate ion-exchanger and poly(vinyl chloride) plasticized with dibutyl phthalate, or like a carbon paste-based electrode containing the same ion-pair and tricresyl phosphate. Properties of these electrodes were studied. When used for direct potentiometric determination of malachite green, the electrodes showed Nernstian responses over the concentration range of $1.0\times10^{-6} - 1.0\times10^{-3}$ *mol l*$^{-1}$. *Their*

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application to the potentiometric titration of malachite green with tetraphenylborate was studied using automated titration mode.

Introduction

Malachite green (MG) belongs to the group of triarylmethane dyes. These dyes are of a chromophore system based on triphenyl methane with the quinoid grouping, in which both electron-donor (free or substituted amino groups, hydroxy groups) and electron-acceptor (carbamide or carbonyl groups) substituents, usually in the para-position to the methane C-atom, are present. Basic triarylmethane dyes are usually prepared in their water-soluble cationic forms, $R_2N-Ar-C(Ar)=Ar=N^+R_2 \rightleftharpoons [R_2N-Ar-C(Ar)-Ar=NR_2]^+$, the charge of the cation being compensated by chloride or other univalent anion. Like most dyes, malachite green (R = methyl, Ar = phenyl) is also known by a number of synonyms, most of these are trade names. The Colour Index [1] contains extensive listing of such synonyms and allocates to each dye a unique number and name which eliminates confusion over trade names (malachite green is indexed under constitution number C. I. 42000, generic name C. I. Basic Green 4). The dye is used extensively as a fungicide [2] and ectoparasiticide in fish farming industry throughout much of the world. Although MG is not licensed for fisheries use, it is still advertised for this purpose. Despite extensive investigations, no effective alternative to malachite green has yet been found [3]. MG is manufactured in significant quantities for the dyeing of materials such as leather, paper and acrylic fibres. The yield of MG from commercial manufacturing synthesis is approximately 65% and there may be significant variations between batches. For this reason, dye manufacturers, who must produce a standard product in terms of its dyeing ability, achieve this by "diluting" down the dry dye with bulking agents such as sodium chloride or sucrose to produce standard dye strength. High quality grades of MG can be produced by inclusion of additional purification stages in production, but even a nominal 100% MG dry powder by analysis can only contain 82% (oxalate) or 95% (hydrochloride), the rest of the weight being the acid component.

However, relatively little information on the analysis of such dyestuffs has been published; the book by Lastovskii and Vainshtein [4] is still a very useful manual. Concerning potentiometric methods for the dyes control [5], a Pungor type ion-selective electrode was prepared and used for the analysis of MG chloride salt [6]. Simple indicator coated-wire type electrodes were also prepared and applied in potentiometric titrations of MG and other cationic dyes against sodium tetraphenylborate [7]. During the progress of ion-selective electrode technology, novel electrodes have been prepared for direct determination of MG. For example, Li and Wang [8] prepared a coated glass electrode using a poly(vinyl chloride) membrane plasticized with dibutyl phthalate containing MG tetraphenylborate as an electroactive ion-exchanger; the electrode was applicable in the concentration range $5.0\times10^{-7} - 1.0\times10^{-4}$ mol l^{-1} for MG with average recovery of 99.6%. MG ion-selective electrodes were also fabricated for determination of phosphorus [9] and catalytic potentiometric determination of tungsten [10] or nitrite [8,11]. In the paper presented here, different ways of preparation of MG ion-selective electrodes are described and their basic characteristics are compared.

Experimental

Apparatus

Potentiometric measurements were mostly performed using a PHM62 pH meter (Radiometer, Copenhagen), equipped with a sensing MG ion-selective electrode in combination with a saturated calomel electrode. Potentiometric titrations were performed using an ATI Orion 960 Autochemistry System (Orion Research, Boston, MA) connected to an HW486 PX2 80 personal computer. In titrations, an RCE-102 Crytur calomel electrode (Monokrystaly, Turnov) of double-junction construction, filled with saturated potassium chloride (inner compartment) and 0.01 M sodium nitrate solution (outer compartment), was used as a reference half-cell.

Reagents and Other Chemicals

All the chemicals were of the analytical reagent grade and double distilled water was used throughout the experiments. Malachite green oxalate (BDH) was used without further purification. Its ca. 10^{-2} M stock solution was prepared by dissolving the appropriate amount in water acidified with acetic acid. A real MG stock solution concentration was determined by potentiometric titration against sodium tetraphenylborate [7]. MG solutions of other concentrations were prepared by further dilution with water.

Sodium tetraphenylborate solution (ca. 5×10^{-3} mol l^{-1}) was prepared by dissolving a weighed amount of the substance (Merck) in water, then adjusted to pH 9 by adding sodium hydroxide solution and completed to the desired volume with water. The resulting solution was standardized potentiometrically against standard 10^{-2} M thallium(I) nitrate solution [12,13].

Poly(vinyl chloride) (PVC) of relative high molecular weight (Fluka) dissolved in tetrahydrofuran (BDH) or cyclohexanone (Analar) was used for the membrane preparation; dibutyl phthalate (BDH) was mostly used as a plasticizer. Other plasticizers were also investigated. Graphite powder (CR5, Tesla, Lanškroun) and tricresyl phosphate (Fluka) were used in case of the carbon paste electrode preparation.

Preparation of Malachite Green Tetraphenylborate

Malachite green tetraphenylborate (MG-TPB) ion-exchanger was prepared by dropwise addition of 0.01 M sodium tetraphenylborate to 50 ml of 0.01 M malachite green solution with continuous stirring. After the reaction was completed (the remaining solution become colorless), the resulting precipitate was filtered, washed several times with distilled water and then dried at 60 °C for 24 hours. The resulting compound was washed with petroleum ether to remove any water and kept dry in a desiccator (m. p. 85 °C).

Preparation of Malachite Green Ion-Selective

Matrix composition for each electrode is given in Table I. For the preparation of coated-wire electrodes (CWEs) based on silver or platinum, a metal wire (1mm diameter) was sealed into the end of a PVC tube. The wire was polished, carefully cleaned in strong ammonia solution, rinsed, carefully dipped in 50% nitric acid for 1 min, rinsed with distilled water but not dried. Then the wire was cathodized against a silver anode at 5 mA cm^{-2} in 0.1 M HCl for 30 s, allowing the bubbles to disperse from the wire, then washed and left to dry [14]. The resulting electrode was dipped in MG-TPB-PVC matrix 15 times, and after each dipping the solvent was evaporated using an air gun. After 24 hours, the solvent was completely evaporated and then the electrode was preconditioned (by soaking it in 10^{-3} M MG solution for 2 h) before use.

For copper and aluminum CWEs, commercially available isolated electrical conductors (1.5 mm thickness) were used for the construction of the electrode after removing the insulator [15]. After polishing, the wire was dipped in MG-TPB-PVC matrix 35 times, and after each dipping the solvent was evaporated using air gun. The solvent was completely evaporated after 2 days and the electrode was conditioned by soaking in 10^{-3} M MG solution for 1 h.

Finally, a commercially available TK Pencil fine Japanese type was used as a graphite-based material for the MG ion-sensitive electrode. The rod was immersed in chloroform for 10 min, formed to the required size and then ignited in a colourless flame for 1 min. After cooling, the rod was mounted into a Teflon tube. The open end of the tube was then connected to a slight vacuum and the other end containing carbon rod was immersed into the cocktail 20 times, and after each immersion the solvent evaporated using an air gun. The electrode was kept dry at room temperature for 24 h and preconditioned by soaking in 10^{-3} M MG solution for 3 h before using.

Table 1 Composition of matrices for malachite green ion-selective electrodes

Electrode	Matrix composition			Solvent, ml
	MG-TPB, mg	PVC, mg	Plasticizer, ml	
Conventional type	51.9	181.2	DBP, 0.176	CH, 6
Ag, Pt CWE	2.2	107.8	DBP, 0.106	THF, 3
Cu, CWE	2.2	107.3	DBP, 0.106	CH, 3
Al, CWE	2.2	97.7	DBP, 0.098	THF, 3
Coated carbon rod	2.2	73.5	DBP, 0.141	THF, 3
Ag/AgCl disc	11.1	103.1	DBP, 0.100	THF, 3
Graphite support	22.0	97.7	DBP, 0.099	THF, 3
CPE	100	0.90	TCP, 0.4	

Mg-TPB, malachite green tetraphenylborate; PVC, poly(vinyl chloride); DBP, dibutyl phthalate; CWE, coated-wire electrode; CH, cyclohexanone; THF, tetrahydrofuran; CPE, carbon paste electrode

A silver pellet (1.1 cm diameter, 2 mm thickness) of spectroscopically pure silver was applied in preparation of another electrode. The electrical contact was effected by attaching it to a copper wire. The electrode was cleaned as in the case of silver CWE and then anodized for 10 – 15 min, rinsed with water and left to dry [14].

For a graphite-paraffin oil electrode, 0.89 g of graphite powder was mixed with 1.2 g of paraffin oil, the produced paste was introduced into a cavity of a Teflon tube and a reference silver wire was then screwed in the paste. For a graphite-PVC electrode, 0.9 g of PVC was dissolved in 5 ml of tetrahydrofuran, then 0.8 ml of dibutyl phthalate was added and 1.2 g of graphite powder was thoroughly mixed with the matrix using a magnetic stirrer for 5 min. After removing of air bubbles, the resulting cocktail was poured into the cavity of a Teflon tube. The solvent was evaporated after 24 h, then the electrode become ready to be coated with the matrix. A volume of 1.2 ml MG-TPB-PVC matrix was poured on the surface of the past using a PVC O-ring. After 24 h the solvent was completely evaporated and the electrode was conditioned by soaking in 10^{-3} M MG solution for 1 h.

General Procedures

Calibration plots for direct potentiometric determination of malachite green. Malachite green aqueous solution (25 ml) was placed into a 50 ml double jacket glass cell kept at 25 °C and acetate buffer (5 ml) was added to adjust the pH value. Then the potentiometric cell containing a MG ion-selective electrode was immersed into the solution. The calibration was made using standard MG solutions in ascending order of concentration, and the potential readings were plotted against MG concentration in logarithmic scale (– log [MG]).

Potentiometric titration of malachite green. An aliquot of the sample solution containing 0.46 – 181.10 μg ml^{-1} MG was pipetted into a 100 ml beaker, pH 6 acetate buffer (10 ml) was added and the volume was completed to 50 ml with water. Sodium tetraphenylborate was used as the titrant, and the titration rate was held constant (determined by a potential change of 10 mV min^{-1}).

Results and Discussion

Characterization of Malachite Green Plastic Membrane-Based Electrodes with an Internal Reference Solution

Having constructed such an electrode, one had to remember that the ion-pair concentration in the membrane should be sufficient to obtain reasonable ionic exchange at the gel layer–test solution interface that is responsible for the membrane potential. However, if such a salt is present in excess, oversaturation occurs in the network of the polymeric membrane hindering the ionic exchange process and leading to unsatisfactory result. With 5 – 20% MG tetraphenylborate added to PVC plasticized with dibutyl phthalate, the electrodes exhibited responses and potential readings with the least square analysis of corresponding data given in Table II. The correlation factors and slopes of the calibration graphs show that the preparation process is reproducible; the average slopes of the calibration graphs ranged between 52.7 and 48.3 mV per decade. The results show that the IV electrode composition (with 12.5% MG-TPB) gives a fairly stable and sensitive membrane indicated by high slope and small standard deviation. Higher concentrations of MG-TPB ion-pair (15 and 20%) cause better sensitivity to higher concentrations of the dye than that to lower value and the membrane become harder with poor physical properties. Lower concentrations of the ion-pair (5 or 7.5%) produce electrodes with more narrow concentration range. The MG-TPB ion-pair concentration of 12.5% seemed to be an optimum from this point of view.

The influence of the choice of the plasticizer on the electrode performances has also been studied (see Table III). It seems that DBP produces the best membrane indicated by the highest slope. Concerning detection limit, all the plasticizers lead to the same effect. It should be noted that Cai *et al.* reported on similar effect of plasticizers [16]. A matrix with composition “IV” was used and applied for preparation of the membrane using tetrahydrofuran or cyclohexanone as solvents for PVC. Each matrix was used for preparation of membranes, cor-

Table II Calibration for conventional type membrane electrodes

Membrane	MG-TPB content, %	Slope, mV/decade	r_k
I	5.0	51.9 ± 1.2	0.998
II	7.5	49.3 ± 1.1	0.999
III	10.0	50.9 ± 0.7	0.999
IV	12.5	52.7 ± 0.7	0.999
V	15	48.6 ± 1.2	0.998
VI	20	48.3 ± 1.5	0.997

Dibutyl phthalate used in all cases to plasticize the PVC membrane; r_k, correlation coefficient; all measurements performed at 25 °C

Table III Calibration characteristics for various membrane plasticizers

Plasticizer	Slope, mV/decade	r_k	Apparent E°, mV	Range, mol l^{-1}
DBP	54.9 ± 0.7	0.990	138.5	$1.0\times10^{-6} - 1.7\times10^{-3}$
DOP	52.7 ± 0.9	0.998	123.3	$1.0\times10^{-6} - 1.7\times10^{-3}$
DDP	48.9 ± 1.6	0.995	107.9	$1.4\times10^{-6} - 1.7\times10^{-3}$
NPOE	51.6 ± 1.1	0.998	117.2	$1.4\times10^{-6} - 1.7\times10^{-3}$
TCP	52.2 ± 1.2	0.997	118.2	$1.4\times10^{-6} - 1.7\times10^{-3}$

DBP, dibutyl phthalate; DOP, dioctyl phthalate; DDP, didecyl phthalate; NPOE, 2-nitrophenyl octyl ether; TCP, tricresyl phosphate

responding electrodes showed responses of 51.4 and 51.5 mV per decade, respectively. Membranes obtained from cyclohexanone solutions were thicker (0.24 mm when compared with 0.14 mm for tetrahydrofuran) giving shorter response times and more stable potential readings.

With regard to the pH effect, potential measurements made at two different MG concentrations (2×10^{-4} and 2×10^{-5} mol l^{-1}) indicated no significant change in the electrode potential in the pH range of 3.5 – 8.3. The time required to achieve a steady potential by rapid tenfold increase of malachite green concentration to the same solution was also measured. The results indicated an average response time of 12 s for $10^{-5} - 10^{-2}$ M MG solutions.

When calibration graph was constructed (Fig. 1), the MG ion-selective electrode prepared using a matrix of 51.9 mg MG-TPB, 181.2 mg PVC and 0.176 ml DBP in 6 ml cyclohexanone and preconditioned by soaking into 10^{-3} M MG solution for 24 h (then stored in deionized water) was used. The electrode showed a response of 53.6 ± 0.5 mV per decade with a constant imitating standard potential of 223.5 mV. The correlation coefficient was 0.9992 within the concentration range of 2.3×10^{-3} – 2.5×10^{-6} mol l^{-1} with detection limit of 1.0×10^{-6} mol l^{-1} and an average response time of 12 s.

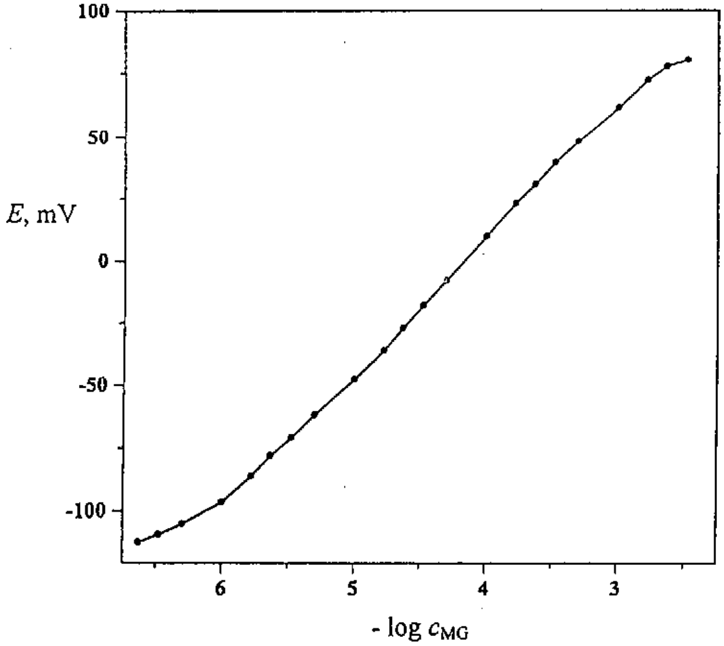

Fig. 1 Calibration dependence for conventional type plastic membrane MG ion-selective electrode

Electrodes Based on Coated Metal Wires or a Carbon Rod

With 1.0 – 12.5% MG–TPB ion-pair complex in a solution of PVC plasticized with DBP, the electrodes exhibited responses and potential readings as shown in Table IV. The preparation process was reproducible. For silver coated-wire ion-selective electrodes, average slopes of calibration graphs were between 66.2 and 52.8 mV per concentration decade. The electrode with a composition denoted "I" gave a fairly stable and sensitive membrane indicated by the best slope with the lowest detection limit. Similar results were obtained with coated copper wire and carbon rod electrodes while other matrices gave higher detection limits. In the case of coated aluminum wire electrode, membrane composition "IV" exhibited the best performance characteristics.

Table IV Calibration characteristics for electrodes of the coated-wire type

Support		Composition			Slope, mV/decade	r_k	Apparent E°, mV	Detection limit $\times 10^6$, mol l^{-1}
		MG-TPB, mg	PVC, mg	DBP, ml				
Ag	I	2.20	107.3	0.106	62.2 ± 1.2	0.998	477.1	1.0
	II	5.51	105.3	0.104	63.9 ± 2.0	0.998	475.9	1.7
	III	11.11	103.1	0.103	66.2 ± 1.7	0.999	433.0	2.3
	IV	16.53	99.9	0.100	52.8 ± 4.0	0.989	421.0	2.3
	V	21.99	97.7	0.098	63.6 ± 1.4	0.997	482.0	1.7
	VI	27.55	94.5	0.095	61.7 ± 0.9	0.998	463.5	1.7
Al	I	2.20	107.3	0.106	50.4 ± 3.0	0.986	-23.9	1.7
	II	11.11	103.1	0.103	51.5 ± 1.1	0.997	-40.8	3.3
	III	16.53	99.9	0.100	51.3 ± 4.0	0.994	-26.6	1.7
	IV	21.99	97.7	0.098	55.7 ± 1.5	0.996	-58.8	1.7
Cu	I	2.20	107.3	0.106	50.7 ± 0.5	0.998	359.0	1.7
	II	5.51	105.3	0.104	66.1 ± 5.7	0.978	393.0	2.3
	III	11.11	103.1	0.103	50.2 ± 0.9	0.999	352.0	3.3
	IV	16.53	99.9	0.100	50.1 ± 0.9	0.998	359.0	3.3
	V	21.99	97.7	0.098	50.1 ± 0.8	0.990	359.0	3.3
C rod	I	2.20	107.3	0.106	49.5 ± 1.1	0.997	492.3	1.0
	II	5.51	105.3	0.104	50.6 ± 0.7	0.997	488.2	1.0
	III	11.11	103.1	0.103	50.6 ± 1.0	0.997	481.2	1.7
	IV	16.53	99.9	0.100	50.7 ± 1.0	0.998	471.1	1.7
	V	21.99	97.7	0.098	50.4 ± 0.9	0.998	486.6	1.7

The influence of the plasticizer on the coated both silver wire and carbon rod electrodes has been studied. The results summarized in Table V indicate that DBP gave the best membrane electrode characterized by the highest slopes and the lowest detection limits. Coated-wire ion-selective electrodes do, in fact, appear to have an internal reference system built into them, albeit fortuitously. Since PVC is permeable to both oxygen and water, an oxygen electrode will be setup at the wire-PVC interfaces, and may function as an internal reference [17]. Attempts at the explanation of the mechanism at the membrane/wire interface and similarity of such systems were mentioned in some references [18,19].

As followed from the measurements done at pH values ranging between 3.5

Table V Influence of plasticizers on calibration characteristic of coated-wire electrodes

Plasticizer	Coated silver wire				Coated carbon rod			
	Slope, mV/decade	r_k	App. E°, mV	DL $\times 10^6$, mol l^{-1}	Slope, mV/decade	r_k	App. E°, mV	DL $\times 10^6$, mol l^{-1}
DBP	58.2 ± 0.7	0.997	368.7	1.0	56.1 ± 1.1	0.999	453.1	1.0
DOP	52.4 ± 1.2	0.996	366.6	1.0	55.0 ± 0.6	0.999	448.1	1.0
DDP	47.1 ± 1.1	0.997	353.6	1.4	49.7 ± 1.0	0.997	405.9	1.4
DOA	51.9 ± 0.9	0.998	365.1	1.0	50.3 ± 1.2	0.997	396.4	2.0
NPOE	51.8 ± 1.2	0.996	315.7	1.4	54.5 ± 0.8	0.998	431.1	1.4
TCP	50.2 ± 0.7	0.998	420.7	1.4	54.3 x 0.5	0.999	557.8	2.0

DL, detection limit; other abbreviations as indicated before

Table VI Calibration characteristics for selected coated-wire electrodes

Support	Composition			Slope, mV/decade	r_k	Apparent E°, mV	Detection limit $\times 10^6$, mol l^{-1}
	MG-TPB, mg	PVC, mg	DBP, ml				
Ag	2.20	107.3	0.106	58.5 ± 0.7	0.999	323.0	0.36
Pt	2.20	107.3	0.106	56.7 ± 0.7	0.998	434.9	1.70
Al	2.20	97.7	0.098	60.1 ± 0.6	0.999	64.8	1.70
Cu	2.20	107.3	0.106	54.1 ± 0.8	0.988	379.8	1.70
C rod	2.20	73.5	0.141	59.7 ± 0.7	0.999	534.7	0.36

and 8.3, such a medium change had a negligible effect on the potential reading of both silver wire-based and coated carbon rod electrodes up to pH 6.5: the potential difference did not exceed ± 2 mV. The potential of platinum-based electrode was stable up to pH 5.0, copper-based electrode potential was stable mostly within all the pH range of 4.5 – 8.3. The coated aluminium wire electrode was more sensitive towards pH variations; its potential was stable within a pH interval of 4.5 – 6.0. Both coated silver wire and carbon rod electrodes showed slightly higher sensitivity towards temperature changes.

The response times of different types of electrodes prepared at the optimum conditions for each were also studied. For the coated silver wire electrode, the average response time was 8 s; the time required to achieve 95% of the total potential change was 4 s. The corresponding values were 23 s and 15 s for platinum-based electrode, 12 s and 6 s for copper-based electrode, 14 s and 8 s for aluminium-based electrode, and 4.5 s and 2 s for coated carbon rod electrode. Before calibration plots were established, all the electrodes were soaked in 10^{-3} M MG solution for about 2 h. It is clear from the characteristic values listed in Table VI that coated silver wire and carbon rod electrodes gave better performance indicated by near-Nernstian slope (58.5 or 59.7 mV per decade, resp.) and the lowest detection limit.

Electrodes with Solid Contact

With 1 – 10% MG-TPB ion-pair complex in a PVC-DBP solution, correlation factors and slopes indicated good reproducibility of the preparation process. For graphite-based electrodes, the average slopes of calibration graphs were 39.2, 48.9, 37.8 and 54.3 mV per decade for 2.5, 5.0, 7.5 and 10 % ion-pair content, respectively. The membrane composed of 10% MG-TPB, 44.3% PVC and 46.7% DBP exhibited a slope of 54.3 ± 1.2 mV per decade and correlation factor of 0.9979. With silver-silver chloride disk electrode, the best results were obtained with a membrane composed of 5% MG-TPB, 46.5% PVC and 48.5% DBP (slope of 56.7 ± 0.6 mV per decade, detection limit of 2.3×10^{-6} mol l^{-1}) while other electrodes gave slopes ranging between 51.8 and 58.4 mV/decade but with higher detection limit around 1.7×10^{-5} mol l^{-1}. It was also found that when cyclohexanone was used as a solvent for PVC, the resulting electrodes did not give any reproducible result due to the slow evaporation of solvent that caused damage of the graphite base. Therefore, tetrahydrofuran was applied in all subsequent experiments.

Influence of the composition of carbon-based supports was also studied; the results are listed in Table VII. For graphite-paraffin oil mixtures, a support with 40% graphite led to electrodes characterized by the highest slope. Pastes containing more than 70% graphite were harder, which caused their cracking. Another disadvantage appeared in that the paraffin oil penetrated through the membrane and contaminated sample solutions. Mixtures of graphite with PVC and DBP were more promising. Temperature hysteresis of such electrodes was limited and independent of the amount of graphite in the composite, which was in a good agreement with previous observations [20]. The response time of the electrode was measured by measuring the time required for the electrode potential to attain a steady reading after successive immersion in different MG solutions each having a tenfold difference in concentration or after rapid tenfold increase in MG concentration. Both results indicate an average response time of 16 s for graphite-based supports and 18 s for a silver-silver chloride support. All the above solid contact electrodes pre-conditioned by soaking in 10^{-3} M MG solution for 1 h and applied in direct potentiometric measurements gave calibration dependences of expected shapes within the MG concentration range of 1.66×10^{-6} – 3.33×10^{-3} mol l^{-1}.

Table VII Calibration characteristic of carbon support–based electrodes

Support composition			Slope, mV/decade	r_k	Apparent $E°$, mV
Graphite, g	Paraffin oil, g				
0.8	1.2		51.1 ± 0.9	0.999	493.6
1.0	1.0		47.6 ± 0.9	0.998	460.1
1.2	0.8		40.9 ± 1.3	0.995	433.2
1.4	0.6		47.6 ± 1.1	0.999	462.9
Graphite, g	PVC, g	DBP, ml			
0.3	1.35	1.30	56.7 ± 2.7	0.992	919.1
0.6	1.20	1.15	53.3 ± 1.6	0.996	804.0
0.9	1.05	1.00	63.4 ± 2.9	0.992	636.5
1.2	0.90	0.87	62.1 ± 2.0	0.995	617.2
1.5	0.75	0.72	54.4 ± 3.3	0.986	575.4

Table VIII Influence of matrix composition on calibration characteristics of carbon paste electrodes

Composition			Slope, mV/decade	r_k	Apparent $E°$, mV	Detection limit × 10^6, mol l^{-1}
MG-TPB, mg	PVC, mg	TCP, ml				
5	245	0.1	51.7 ± 1.3	0.997	349.2	1.4
15	235	0.1	49.6 ± 1.2	0.997	331.9	1.4
20	230	0.1	52.2 ± 0.6	0.999	331.3	1.0
25	225	0.1	52.6 ± 0.7	0.999	364.8	1.0
35	215	0.1	53.1 ± 1.0	0.998	352.0	2.0
40	210	0.1	45.8 ± 1.1	0.997	313.1	1.4

Carbon Paste Electrodes

Influence of the carbon paste composition was studied using pastes prepared as described elsewhere [21]. Characteristic values for pastes composed of carbon

Table IX Influence of pasting liquid on calibration characteristics of carbon paste electrodes

Plasticizer	Slope, mV/decade	r_k	Apparent E°, mV	Detection limit $\times 10^6$, mol l^{-1}
DBP	50.4 ± 0.6	0.996	348.7	2
DOP	44.6 ± 1.1	0.997	348.2	2
NPOE	42.7 ± 0.8	0.997	342.3	1.3
TCP	51.5 ± 1.3	0.997	364.1	1

Table X Titrations of malachite green against sodium tetraphenylborate

Electrode	Mediator	Potential change		Steepness, mV ml^{-1}	Titration time, min
		Total, mV	Break, mV		
Coated Ag	DBP	322	157	1035	11
	DOA	295	87.2	585	16
Coated C rod	DBP	315	158	1099	15
	DOA	313	95	440	19
CPE	TCP	241.9	133.4	685	8
Conventional	DBP	246.5	132.6	893	8
	DOP	227	72.8	502	9
	NPOE	218	112	726	9
	TCP	235	93	638	12

powder, PVC, MG-TPB and tricresyl phosphate are listed in Table VIII. Other pasting liquids recommended recently [22] were also examined (see Table IX). With the expection of dioctyl adipate, which produced electrodes of very bad properties, all the others exhibited acceptable responses but tricresyl phosphate could be classified as the best mediator. For 2×10^{-6} and 2×10^{-5} M MG solutions, potential readings remained stable (± 2 mV) in the pH range of 3.5 – 5.5. The best response was observed in solution buffered to pH 6, which was therefore preferred for calibration. Potential measurements showed high sensitivity towards temperature changes (studied in a range of 20 – 70 °C). The response time determined by measuring the time required to achieve a steady potential by rapid tenfold increase in MG concentration showed an average of 7 s. The equilibrium voltage was stabilized during much shorter times; this could probably be caused by a quick diffusion of ions into the very thin film of pasting liquid coated onto small particles of carbon powder, as confirmed by microscopic studies [23].

Although the potentiometric titration technique consumes longer time and larger amount of titrants, it has an advantage of high accuracy than direct potentiometry. Titrations of MG solutions against sodium tetraphenylborate titrant monitored with MG ion-selective electrodes were therefore investigated as well. Titrations of 2×10^{-4} M MG (25 °C, pH 6 acetate buffer) were carried out using different electrodes (Table X); typical output of the titrator is given (Fig. 2).

When the liquid and/or plastic membrane electrodes are used to monitor the titrations based on ion-pair formation, the magnitude of both the potential break and sharpness at the inflexion point of the titration curve is predetermined by the

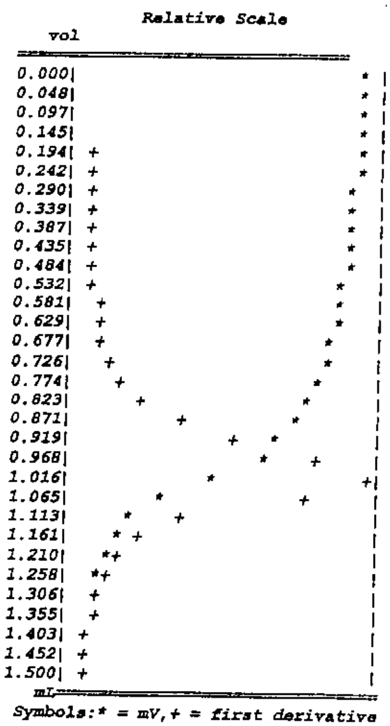

Fig. 2 Example of automated potentiometric titration of malachite green against sodium tetraphenylborate using coated silver wire MG ion-selective electrode: Sample volume, 4.00 ml; titrant, 0.009621 M $NaBPh_4$; constant increment, 0.100 ml; stability criterion, 10.0 mV min^{-1}; prestirring, 10.0 s; continuous stirring; acetate pH 6 buffer. An output of the Orion 960 Autochemistry System: Sample concentration, 0.00244 mol l^{-1}; end-point volume, 1.012 ml (−187.6 mV)

solubility of the corresponding ion-pair compound and connected also with the extractability of the ion-pair into the membrane solvent [24,25]. It is interesting that the best parameters were observed for electrodes of the coated-wire type containing dibutyl phthalate. The possibilities of determining of the real dye content in the MG oxalate preparation were therefore tested using a coated silver wire/(PVC+DBP) electrode. The stock solution of malachite green and tetraphenylboarate were diluted to 10-, 100-, and 1000-fold compared with their initial concentrations, and the titration curves were recorded. The dilution caused both the steepness and the overall potential jump of the titration curve to decrease, of course, but the potential jumps were surprisingly well pronounced for titrations of 10 mg and 1 mg of the MG sample and were usable even for 0.04 mg, corresponding titration curves were well reproducible. In the concentration range of 0.46 – 181.1 μg ml^{-1}, the average recovery was 54.66% with relative standard deviation of 2.0%.

Conclusion

First, it is necessary to conclude that each individual electrode represents a unique compartment with its individual characteristics different from each to other, thus the values of slopes and responses given in tables should be comprehended as informative only. From the electrodes prepared in this study, the best seemed to be both coated silver wire and coated carbon rod, resp., characterized by near-Nernstian slopes and the lowest detection limit. It should be mentioned that both the electrodes were applied in kinetic catalytic determination of trace nitrite based on the oxidation of malachite green with bromate [11]. The absence of an internal solution in solid contact ion-selective electrodes allows these types of electrode to be used in any position (horizontally, inverted, etc.) and in a variety of situation (microgravity, rotation, vibration, etc.). In addition, due to the elimination of the internal reference solution, these electrodes have certain advantages such as small size, lower coast of production and ability to operate in high-pressure environments where the symmetric ion selective electrodes might be damaged [26]. Even though the heterogeneous membranes with internal reference solution give good results and good stability in different pH and temperature values, they still have certain inherent limitation. They are mechanically complicated and thus difficult to manufacture in small size, the internal reference solution increase the system impedance and due to internal compartment they cannot stand with higher pressure. Finally, the occurrence of a single solution/membrane interface in all solid-state electrodes diminishes the risk of leashing of the sensing system confined within the membrane.

Carbon substrate-based electrodes gave good results but those prepared using paraffin oil caused contamination of samples due to penetration of the oil through the membrane, this is why those prepared with addition of PVC and plasticizers were preferred. Carbon paste electrodes showed much lower Ohmic resistance and quicker time response, which was appreciated especially when they were applied to monitor titration procedures.

Acknowledgements

Financial supports of the Ministry of Education, Youth and Sports of the Czech Republic (project No. 253100002) and of the Grant Agency of the Czech Republic (project No. 203/99/0044) are gratefully acknowledged.

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