Fresenius J Anal Chem (1998) 360 : 659–663

ORIGINAL PAPER

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Construction and evaluation of ion-selective electrodes for potassium and calcium with a summing operational amplifier. Application to wine analysis

Received: 27 June 1997 / Revised: 29 September 1997 / Accepted: 3 October 1997

Abstract Electrodes selective to potassium and calcium with improved senstivity were constructed like conventional electrode (ISEs), but used an operational amplifier to sum the potentials supplied by the four membranes (ESOAs). The results obtained during the evaluation of their working characteristics were compared to those obtained by conventional ISEs and were found to be similar, but with higher precision. The electrodes were used in the potentiometric determination of potassium, calcium and magnesium in wines. The results given by ESOAs were more precise than those from ISEs. The results obtained by potentiometry were in good agreement with those from AES for potassium and AAS for calcium and magnesium.

Introduction

The usefulness of ion-selective electrodes (ISEs) is widely recognized today and their properties and characteristics make them very attractive analytical tools. These ISEs are suitable for certain applications such as food analysis, but their use requires some precaution like ensuring that the ion to be measured is in an uncomplexed state, that major interferences have been removed, and that pH and ionic strength have been adjusted. The application of potentiometry to wine analysis has been reviewed [1].

The fact that ISEs present a constant sensitivity over a wide interval of concentrations, albeit a great advantage in many circumstances, also has a peculiarity. For example, a measurement error of ca. ± 0.5 mV corresponds to a relative error in concentration of ca. 2% in the case of electrodes sensitive to monovalent species, and of ca. 4% for those sensitive to divalent ones [2–4]. Several solutions to this kind of problem have been suggested by some authors on the basis of cells connected in series [5–7] or alternatively by totalling the potentials of two conventional electrodes immersed in the same vessel [8–10].

This work refers to the construction of two ion-selective electrodes, sensitive to potassium and calcium, which comprises four sensor membranes placed in the same electrode body with summing operational amplifiers (ESOAs), which are more sensitive (quadruple slope) than conventional electrodes.

The construction, a mobile conductor without an inner reference solution in which PVC membranes are directly applied onto a conductive epoxy resin support used in this work was the same as that previously reported [11]. We have constructed ISEs and ESOAs for potassium and calcium using valinomycin and calcium bis-di-[4-(1,1,3,3-tetramethylbutyl) phenyl] phosphate, respectively, as sensors. The choice of these sensors is justified by the fact that they provide good quality electrodes.

An evaluation of the behavior of all the units constructed and their applicability to the sequential determination of potassium by multiple standard addition and calcium and magnesium by sequential potentiometric EDTA titration in different types of wines is reported. These species were also determined for comparative purposes by AES (for potassium determinations) and AAS (for calcium and magnesium determinations), according to the Association of Official Analytical Chemists [12] and the Office International de la Vigne et du Vin [13], respectively.

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Experimental

Apparatus and electrodes

The potentials were measured with a Crison (2002) digital potentiometer (± 0.1 mV sensitivity). Electrodes switchers of the same brand were coupled to the potentiometer. An Orion (Autochemistry System 960) automatic titrator was used.

The AgCl/Ag double-junction reference electrodes were Orion (90-02-00). A 0.1 mol/L sodium nitrate solution was placed in the outer compartment. The solution used in the inner compartment was the same as provided with the reference electrode (Orion 90-02-00) for both determinations. For pH determinations, namely those used for tracing the Reilley diagrams, an Orion (91-02-00) combined glass electrode was used.

Measurements were carried out in double-walled cells at 25.0 ± 0.2° C by means of a thermostatized water bath Selecta (Tectron 3473100).

A Dr. Bruno Lange flame photometer (M6a) for the AES determinations and a Perkin Elmer (2380) for the AAS determinations were used.

Reagents and solutions

Analytical grade reagents were used without further purification throughout. The solutions were prepared with distilled and deionized water with a conductivity of less than 0.1 $\mu S \cdot cm^{-1}$.

The potassium stock solutions were prepared by dissolving potassium chloride, which had previously been oven-dried at 110° C for 24 h. The calcium and magnesium stock solutions were obtained by dissolving the respective chlorides and titrating them with EDTA solution (previously standardized with zinc oxide, reagent grade, ignited for 20 min at 1000° C).

When necessary, the working solutions of the three cations were prepared by rigorous dilution of the corresponding stock solution.

Construction of the ISEs and ESOAs

The construction process was a modification of that given in [11]. For cost reasons, the silver-based conductor was replaced by a mixture (1 : 1.2 W/W) of graphite powder (Merck, ref. 4206) and a non-conductive epoxy resin (1 g of Araldite M with 0.4 g of hardener HR, Ciba-Geigy). At the extreme of the electrode body, consisting of a perspex tube (external ∅ 12 mm, internal ∅ 10 mm, length 15 cm), a septum of the same material, that divides it into four equal parts, was applied. The conductor support, consisting of a mixture of epoxy resin and graphite, and four shielded cables, were placed in these compartments.

The support was left to harden overnight in an oven at 50–60° C. Then, a 2 mm deep cavity was cut out, in which we placed the membrane in a similar manner as that previously described for conventional electrodes [14].

The membrane used in the construction of the ISEs and the ESOAs consisted, in the case of the units sensitive to the potassium, of 1% sensor (valinomycin), 66% of the solvent mediator (bis(2-ethylhexyl)sebacate) and 33% of PVC, dissolved in tetrahydrofuran, and in the case of calcium, of 3.6% sensor (calcium bis-di-[4-(1,1,3,3-tetramethylbutyl)phenyl] phosphate), 65.4% of the mediator solvent (di-n-octylphenyl phosphonate) and 31% of PVC solved in tetrahydrofuran. All the reagents were from Fluka.

After successive applications of the membranes onto the solid conductive support, the different units were left to dry for two days at room temperature, to guarantee a complete tetrahydrofuran evaporation. After preparation, they were conditioned for 3 days in a 0.1 mol/L solution of the primary ion.

The summing device was composed of four voltage following stages implemented and calibrated so that the potential would be equal to the sum of potentials supplied by each of the voltage followers. The whole setup was installed in a metallic box together with a symmetric power supply source.

Proposed analytical procedures

Sample treatment. An aliquot of 50 mL of wine sample was evaporated in a 75 mL flat-bottom porcelane dish on a water bath to syrupy consistency. The residue was heated in an oven at 525 ± 25° C for 15 min and cooled to room temperature. If the carbonization step had not been completed, 5 mL of deionized water was added and the whole process was repeated. The ashes obtained were dissolved with 10 mL of a 2 mol/L HCl solution. Approximately 25 mL of deionized water was added and the solution was boiled for 2 min. After cooling, the solution was diluted to 50 mL with deionized water. In case of sweet wines, the addition of a few drops of pure vegetable oil before the sample was introduced into the oven was recommended to avoid over-flow [15].

Sequential potentiometric determination of potassium, calcium and magnesium. An aliquot of 10.00 mL of treated wine sample was pipetted into a 100.0 mL volumetric flask; 10 mL of a 1.0 mol/L sodium nitrate solution (ISA) and 20 mL of a 0.1 mol/L acetic acid/sodium acetate buffer solution (pH 4.5) were added and made up to volume with deionized water. The solution was transferred to a plastic beaker, the reference and potassium and calcium ESOAs were immersed, a 0.1 mol/L standard potassium chloride solution was successively added from the reservoir and the potassium concentration was automatically calculated. Afterwards, 5 mL of a 1 mol/L ammonia/amonium chloride buffer solution and 5 mL of a 0.1 mol/L acetylacetone solution were added. Finally a 0.01 mol/L EDTA solution, used as titrant reagent, was automatically dispensed. The tritation end-points were directly calculated by the automatic titrator.

Results and discussion

General characteristics of the potassium and calcium ESOA's

The response characteristics were evaluated by repeatedly preparing calibration curves for solutions between 10^{-6} and 10^{-1} mol/L, covering the linear and non-linear response zones. The ionic strength was adjusted to 0.1 mol/L with NaCl, and the lower limits of linear response, the practical limits of detection, the slopes and the reproducibility of the potential values were established [16].

The response time was determined by spiking a dilute solution (10^{-5}, 10^{-4} and 10^{-3} mol/L) with a more concentrated one so as to obtain a × 10 concentration jump and recording the time required for a stable potential (± 0.1 mV).

The extent of the proton and hydroxide interferences was evaluated by measuring, at different pH values, the potentials of the electrodes in solutions of constant concentrations of the primary ions (10^{-4}, 10^{-3}, 10^{-2} or 10^{-1} mol/L) and tracing the Reilley diagrams.

The potentiometric selectivity coefficients were determined for 3 concentration values of the primary ions and various cation interferences (10^{-4}, 10^{-3} and 10^{-2} mol/L) by using the separated solutions method.

The evaluation of the working characteristics of the ESOAs for potassium and calcium was performed simultaneously with ISEs constructed with conventional shape, using the same type of membranes. Some of the results obtained are shown in Table 1. This parallel study proved that the behavior of the ESOAs was, as a whole, similar to the corresponding ISEs with the same type of membranes, except for the slope which was ca. 4 × that of the conventional ISEs.

The electrodes showed an initial drift of potential and the stability only appeared if the potassium and calcium ISEs and ESOAs had been conditioned for three days in

10^{-3} mol/L solutions of the corresponding primary ions. The establishment of a constant electrode potential required a period to stabilize the internal reference potential in the graphite conductive epoxy-PVC boundary by means of the O_2-H_2O couple, as has been previously suggested [17, 18].

All the units had a long lifetime (generally greater than 12 months), which is quite good for electrodes whose membranes are based on mobile carrier sensors. This is probably due to the absence of an internal reference solution and because the membrane is directly applied onto the conductive support [11].

Sequential determination of potassium, calcium and magnesium in wines

For potassium determination the multiple standard addition method was carried out. The same ISA solution and double junction compartment filled with a 0.1 mol/L sodium nitrate solution was used for the three determinations.

It is not feasible to perform calcium and magnesium sequential potentiometric titrations directly to two endpoint potentials, since the potentials in the equivalence points will vary with the concentration of calcium and magnesium. In this work calcium and magnesium in wines were titrated for the first time, using ISEs and ESOAs selective to the calcium ion and EDTA as the titrant in the presence of acetylacetone, as proposed for the determination of these cations in drinking water [19] and in parenteral and hemodialysis solutions [14]. The ratio between EDTA's conditional stability constants for calcium and magnesium was increased by the use of the acetylacetone, so that two well defined inflection points were obtained on the titration curve.

Sequential potentiometric titrations were carried out by using an automatic titrator, whose dynamic parameters were adjusted using synthetic solutions prepared in the laboratory with compositions similar to those of the wine samples [21]. Then several wine samples, whose calcium and magnesium concentrations had been previously determined by the reference techniques, were titrated by using different magnesium/acetylacetone ratios and buffer solutions. The best results were obtained with 1/15 ratio and ammonia/ammonium chloride buffer solution. Since high concentrations of acetylacetone affect the life time of the electrodes, the wine samples were diluted ten times.

The data (Table 2) confirm that the potentiometric methods had good precision and accuracy. The ESOAs had better precision and recoveries compared to conventional ISEs and the reference techniques when simultaneously applied to the determination of all the three cations. To test whether the potentiometric and reference methods differ in their precision, a significance F test (two-tailed test) was carried out. The calculated F-values for all the wine samples were less than the critical F-value; so there is no significant difference between the two standard deviations at the 95% confidence level.

Thirty-six red, rosé, and white wine samples were analyzed in duplicate. The results showed mean concentrations of 857 mg/L potassium, 92 mg/L calcium and 103

Table 1 General working characteristics of the ISE's and ESOA's

Characteristics	Potassium		Calcium	
	ISE	ESOA	ISE	ESOA
Lower limit of linear response [mol/L]	2.0×10^{-5}	1.4×10^{-5}	3×10^{-5}	1.2×10^{-5}
Practical limit of detection [mol/L]	3.0×10^{-6}	2.2×10^{-6}	5×10^{-6}	3.5×10^{-6}
Slope (mV/log C)	57.2 ± 1.1	234.0 ± 1.3	28 ± 1.1	115.5 ± 1.6
Response stability ($mV \times d^{-1}$)	1.1	1.2	1.1	1.2
Response time (s)				
10^{-3} to 10^{-2} mol/L	20	20	50	48
10^{-4} to 10^{-3} mol/L	27	27	50	50
Working pH range				
10^{-3} mol/L	3.5–11	3.5–11	5–10	5–10
10^{-4} mol/L	4 –11	4 –11	5– 9.5	5– 9.5
Lifetime (months)	> 12	> 12	> 12	> 12

Potentiometric selectivity coefficients ($\log K^{pot}_{X,I}$)								
X	10^{-4} mol/L	10^{-3} mol/L	10^{-4} mol/L	10^{-3} mol/L	10^{-4} mol/L	10^{-3} mol/L	10^{-4} mol/L	10^{-3} mol/L
Li^+	–1.9	–3.0	–1.9	–2.9	–5.1	–5.0	–5.1	–5.0
Na^+	–2.0	–2.8	–2.6	–2.5	–5.0	–5.1	–5.0	–5.1
K^+					–5.4	–5.4	–5.4	–5.4
NH_4^+	–1.5	–1.7	–1.5	–1.7	–6.0	–4.9	–6.0	–4.8
Ca^{2+}	–3.7	–3.9	–3.8	–4.0				
Mg^{2+}	–4.0	–4.4	–4.0	–4.4	–0.9	–1.7	–1.0	–1.8
Ba^{2+}	–3.8	–4.3	–3.8	–4.2	–1.1	–2.3	–1.1	–2.3

Table 2 Results obtained with ISE's and ESOA's for the determination of potassium by the multiple standard additions method and for the determination of calcium and magnesium by sequential potentiometric titration

Type of wine	Reference Method[a]		ISE's				ESOA's			
	X[b]	R[c]	X[b]	R[c]	RE[d]	F	X[b]	R[c]	RE[d]	F
Potassium determination										
Red	1276 ± 15.3	103.6	1 269.7 ± 12.7	101.7	–0.6	1.46	1278.8 ± 10.2	101.3	+0.2	2.24
Rose	441.0 ± 3.5	99.8	437.6 ± 3.1	99.8	–0.8	1.33	439.5 ± 2.2	100.4	–0.3	2.58
White	461.7 ± 4.5	98.6	469.1 ± 4.2	102.7	+1.6	1.76	466.4 ± 2.8	100.4	+1.0	2.58
Calcium determination										
Red	100.0 ± 1.5	100.5	99.5 ± 1.6	104.0	–0.5	1.14	99.7 ± 0.7	103.4	–0.3	1.78
Rose	124.8 ± 1.7	98.5	125.9 ± 1.4	101.9	+0.9	1.59	125.0 ± 0.9	101.8	+0.2	2.41
White	125.0 ± 2.0	100.0	124.6 ± 1.7	102.1	–0.3	1.32	125.3 ± 1.0	99.9	+0.2	2.55
Magnesium determination										
Red	120.0 ± 1.9	98.2	117.9 ± 2.0	99.0	–1.8	1.07	118.1 ± 1.8	100.4	–1.6	1.15
Rose	111.5 ± 2.0	98.4	110.6 ± 2.2	98.6	+0.8	1.19	112.3 ± 1.8	98.8	+0.7	1.22
White	119.5 ± 1.7	98.1	118.2 ± 1.9	97.6	–1.1	1.22	120.3 ± 1.6	98.9	+0.7	1.14

[a] Atomic emission spectroscopy for potassium and atomic absorption spectroscopy for calcium and magnesium
[b] Mean potassium, calcium and magnesium concentration and standard deviation (mg/L)
[c] Mean spike recovery (%)
[d] Relative error of the potentiometric method versus the reference method (%)
The critical F-value, considering a 95% of confidence level and 10 degrees of freedom, for a two-tailed F-test, is 3.72

Table 3 Parameters of the equation $C_r = S\ C_p + C_o$ for comparing the results (mg/L) obtained by the reference methods (C_r) and by the proposed potentiometric methods (C_p) for the determination of potassium, calcium and magnesium in wines

Species determined	ISE's				ESOA's			
	C_o	S	r	t	C_o	S	r	t
Potassium	2.71 ± 0.72	0.996 ± 0.012	0.995	58.10	1.88 ± 0.53	0.997 ± 0.007	0.998	92.06
Calcium	1.82 ± 1.15	0.983 ± 0.014	0.995	58.10	1.23 ± 0.78	0.992 ± 0.010	0.998	92.06
Magnesium	1.17 ± 1.74	1.005 ± 0.018	0.993	49.02	–0.10 ± 1.23	1.019 ± 0.013	0.997	75.11

The tabulated *t*-value, considering a 95% of confidence level and 34 degrees of freedom, is 2.03

mg/L magnesium. The data calculated by regression analysis of the results obtained are shown on Table 3. The confidence limits of the slope, intercepts of the regression lines and the *t*-values for the correlation coefficients at a 95% confidence level and n-2 degrees of freedom were also determined.

Taking into account that these data must be considered in relation to the concentration values in the samples, it is possible to state that the calculated slope and intercept do not significantly differ from the ideal values of 1 and 0, respectively. Thus there is no evidence of a systematic difference between the proposed and the reference methods. From the correlation coefficients, the t-values calculated were always greater than the tabulated t-value (2.03); so significant correlations exist between proposed and reference methods.

Conclusions

The potassium and calcium ESOAs present good working characteristics similar to those of conventionally-shaped electrodes. Their increased sensitivity is due to the sum of the potentials supplied by the four membranes they incorporate, without however a decrease in the potential stability.

From the results obtained it can be concluded that the use of ESOAs for the determination of potassium, calcium and magnesium in wine samples is preferable to the use of ISEs as it gives better values of precision and accuracy, similar to those obtained by the application of the reference methods.

Finally, it should be pointed out that this construction procedure can also be applied to the preparation of ESOAs sensitive to other species, as long as there is an appropiate sensor system and they can be immobilized in PVC.

Acknowledgements The authors gratefully acknowledge the financial support of Departamento de Educación, Universidades e Investigación del Gobierno Vasco, Spain (Project: PI 95/38).

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