

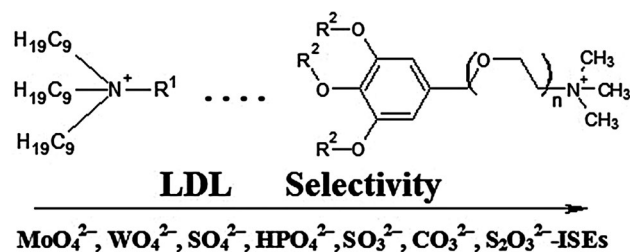
Ion-selective electrodes based on long-chain quaternary ammonium salts with enhanced steric accessibility, and their application for determination of hydrophilic double-charged inorganic anion

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Abstract The effect of long-chain quaternary ammonium salts' exchange center steric accessibility and presence of a neutral anion carrier, 4-(trifluoroacetyl)benzoic acid heptyl ester, upon analytical characteristics of ion-selective electrodes reversible to molybdate, tungstate, sulfate, hydrogen phosphate, sulfite, carbonate and thiosulfate anions, has been studied. When the most sterically hindered quaternary ammonium salts, trinonyl octadecyl ammonium bromide, is replaced by one of the salts with the accessible exchange center, the selectivity is altered, the magnitude of the selectivity coefficient change being determined by the nature of the interfering ion. Thus, for carbonate- and sulfate-selective ISEs with hydrophobic thiocyanate ions as interference, the effect achieved is 6–8 orders of magnitude, while with nitrate ions as interference it is 3.4–5.7 orders, and for such hydrophilic interference ions as sulfate, chloride and oxalate, it is even less. Replacing trinonyl octadecyl ammonium bromide with a sterically accessible ammonium salt improves lower detection limit generally by 1–2 orders, while for sulfite and thiosulfate ISEs the effect is only 0.3–0.95 orders. The procedures for determination of sulfate, sulfite and carbonate ions in real objects (mineral water, dried fruits) have been proposed. They are simple, reasonably accurate, require only widely available equipment and can be recommended for use in chemical and food industries.

Graphical Abstract



Keywords Ion-selective electrode · Quaternary ammonium salt · Steric accessibility · Neutral anion carrier

Introduction

Sulfite, molybdate, tungstate, hydrogen phosphate, carbonate, thiosulfate and sulfate ions occur in natural and/or waste waters. They are also used in laboratory practice as corresponding salts; in addition, sulfites, sulfates, hydrogen phosphates, hydrogen carbonates or carbonates are ingredients of food products. Methods used for their determination include gravimetric analysis, titration, capillary electrophoresis, HPLC, chemiluminescence analysis, extraction photometry, etc. The downside of chromatography, however, is high cost of equipment and complicated sample preparation; chemiluminescence and extraction photometry methods imply using volatile and toxic organic solvents and specialized reagents; gravimetric analysis is laborious and time-consuming.

For contrast, ionometry, with its many promising features such as simple sample preparation, applicability for murky and colored solutions, rapidity, wide working concentration range, low equipment cost, appears to be the

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method of choice in many cases. The additional important advantage is simplicity of making the membranes and ISEs themselves, making them available for any laboratory.

The reviews (Ganjali et al. 2007; Gupta 2010; Bühlmann and Chen 2012) discuss film and solid contact ISEs based on various ionophores. It should be noted that no data is given on film ISEs reversible to tungstate and thiosulfate ions. More attention is given to sulfate, hydrogen phosphate and carbonate ISEs, but for the most part, electroactive compounds used in their design are not currently commercially available. Very few ISEs reversible to molybdate and sulfite ions are mentioned in the literature (Hutchins et al. 1994; Badr et al. 1995; Gupta et al. 2002; Wang et al. 2007). In addition, phosphate and molybdate electrodes cited in the review and articles (Gupta et al. 2002; Gupta 2010; Wang et al. 2007) have too high detection limit (about 1×10^{-5} M); and working pH ranges for molybdate ISEs (4.9–11.3; 5.4–10.5) are somewhat doubtful because in acidic media molybdate ions undergo hydrolysis giving polyanions.

It has been known (Rakhman'ko et al. 1991) that the anion selectivity for quaternary ammonium salts (QAS) parallels the extraction Hofmeister series: $\text{ClO}_4^- > \text{SCN}^- > \text{BF}_4^- > \text{I}^- > \text{NO}_3^- > \text{Br}^- > \text{Cl}^- > \text{Ac}^- > \text{SO}_4^{2-} > \text{F}^- > \text{OH}^- > \text{H}_2\text{PO}_4^- > \text{HPO}_4^{2-} > \text{PO}_4^{3-}$. Long-chain QAS have proved themselves as promising analytical reagents both for use in extraction photometry and for designing anion-selective electrode. One of their distinctive features is low extraction capacity toward hydrophilic double-charged anions, due to strong hydration of the latter and steric hindrance by long hydrocarbon chains connected to nitrogen atoms, preventing the approach of two cations at once to a double-charged ion.

Sulfite, molybdate, tungstate, hydrogen phosphate, carbonate, thiosulfate and sulfate ions are all hydrophilic and so have low affinity to QAS normally used in electrode PVC membranes as electroactive compounds. The above, however, is true only for QAS cations with all four long-chain (propyl or longer) alkyl groups at the nitrogen atom. Therefore, testing new QAS with the sterically accessible exchange center is of much interest.

Here we report the effect of QAS exchange center steric accessibility upon analytical characteristics of ISEs having been studied on the series of QAS including ones with the highest up-to-date accessibility synthesized for the first time specially for this research, such as 3,4,5-*tris*-dodecyloxybenzyl(oxyethyl)_n trimethyl ammonium chloride ((oxyethyl)_nTM), where $n = 2-4$; and 4-(3,4-*bis*-hexadecyloxyphenyl)butyl trimethyl ammonium bromide (BHPBTM). In addition, optimized membrane compositions have been found and some procedures for anion determination in real objects have been developed.

Experimental

ISE membranes have been made according to a standard procedure (Nikol'skii and Materova 1980) and included the following ingredients (% w/w): (poly)vinyl chloride (Fluka AG)—33, QAS ion exchanger—5 (2, in some cases for the carbonate ISE), neutral carrier (4-trifluoroacetylbenzoic acid heptyl ester, TFABAHE)—20 (10, for the carbonate ISE), plasticizer—up to 100. Tetrahydrofuran (Fluka AG) has been used as a solvent.

3,4,5-*tris*-Dodecyloxybenzyl(oxyethyl)_n trimethyl ammonium chloride ((oxyethyl)_nTM), 4-(3,4-*bis*-hexadecyloxyphenyl)butyl trimethyl ammonium bromide (BHPBTM), trinonyl octadecyl ammonium bromide (TNODA), tributyl 3,4,5-*tris*-dodecyloxybenzyl ammonium bromide (TB), 3,4,5-*tris*-dodecyloxybenzyl triethyl ammonium bromide (TE), 3,4,5-*tris*-dodecyloxybenzyl triethyl ammonium bromide (TM) have been used as ion exchangers; dibutyl phthalate (DBP, Sigma-Aldrich), didecyl phthalate (DDP), 1-bromonaphthalene (1-BN) p.a., *o*-nitrophenyl decyl ether (*o*-DNPE), bis(2-ethylhexyl) decanedioate (BEHD) as plasticizers. Solutions for ionometry have been prepared from $\text{Na}_2\text{SO}_3 \times 7\text{H}_2\text{O}$ p., $\text{Na}_2\text{MoO}_4 \times 2\text{H}_2\text{O}$ p.a., $\text{Na}_2\text{WO}_4 \times 2\text{H}_2\text{O}$ p.a., $\text{Na}_2\text{HPO}_4 \times 2\text{H}_2\text{O}$ p., NaHCO_3 p.a., $\text{Na}_2\text{S}_2\text{O}_3$ p.a., K_2SO_4 p., AgNO_3 puriss., H_3PO_4 p., ammonia water solution puriss., ascorbic acid pharm., KCl p.a., NaBr p., KNO_3 puriss., KNCS p., $\text{K}_2\text{C}_2\text{O}_4 \times \text{H}_2\text{O}$ p.a., HCl p.a., iodine p.a., soluble starch, $\text{Ba}(\text{NO}_3)_2$ p.a.

Synthetic procedures for QAS preparation have been described in Akayeu (2005) and Akayeu and Stanishevskii (2017). Structures of new sterically accessible QAS and the neutral carrier used are given in Fig. 1.

All newly made membranes have been soaked for 1–2 days in 1×10^{-1} M solutions of the corresponding salts. The mixture of 1×10^{-2} M of the corresponding ion and 1×10^{-3} M of potassium chloride was used as an internal solution for all ISEs. In sodium hydrogen phosphate, molybdate and tungstate solutions, pH was made about 10 ± 0.2 , in the sodium hydrogen carbonate solution about 8.0 ± 0.1 by diluting it with ammonia solution; sodium sulfite solutions were prepared on the background of 1×10^{-2} M ascorbic acid neutralized by ammonia to pH 7.5 ± 0.1 ; in sodium sulfate solutions, pH was made about 3.2 ± 0.1 , in sodium thiosulfate solutions—about 5.6 ± 0.1 , using dilute phosphoric acid. The same pH values were kept also in the interfering ion solutions while studying the selectivities of ISEs developed (except potassium oxalate solution, there pH was kept at 5.3 ± 0.1 , using phosphoric acid solution, when the sulfate ISE was studied).

ISE calibration was performed both by double dilution method and consecutive dilution method, and for the

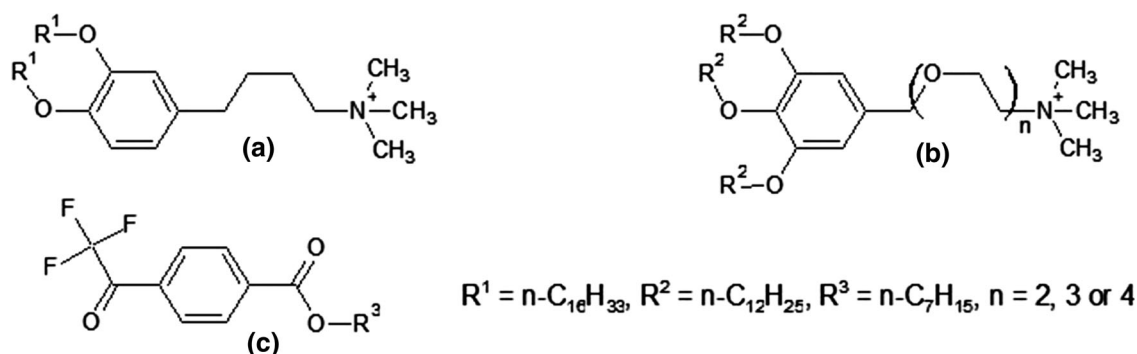


Fig. 1 Structures of some used QAS cations and the neutral carrier: **a**—BHPBTM; **b**—(oxyethyl)_nTM; **c**—TFABAHE

carbonate ISE it has been done by sodium hydrogen carbonate solutions, to avoid the influence of strongly basic OH[−] ions. Activities of carbonate ions in sodium hydrogen carbonate solutions were calculated by the formula (Shin et al. 1999):

$$a(\text{CO}_3^{2-}) = \frac{K_1 K_2 C(\text{HCO}_3^-) f_{\text{HCO}_3^-}}{K_1 K_2 + K_1 a_{\text{H}^+} + a_{\text{H}^+}^2}, \quad (1)$$

where K_1 and K_2 are dissociation constants of carbonic acid; $C(\text{HCO}_3^-)$ is brutto concentration of all carbonate forms in the solution, M; a_{H^+} is activity of H⁺; and $f_{\text{HCO}_3^-}$ are activity coefficients for HCO₃[−] ions in the solution calculated by the Debye–Hückel equation (Dean 1999) (for 20 °C).

Activities of molybdate, tungstate, thiosulfate, hydrogen phosphate and sulfate ions in calibration solutions were also calculated according to Debye–Hückel theory (Dean 1999).

Activities a (activity potential) for sulfite ions were calculated by the formula:

$$p\alpha(\text{SO}_3^{2-}) = p\alpha + pC(\text{SO}_3^{2-}) + pf(\text{SO}_3^{2-}), \quad (2)$$

where α is molar fraction of sulfite ions calculated using Hydra-Medusa software; $f_{\text{SO}_3^{2-}}$ are activity coefficients for SO₃^{2−} ions in the solution calculated by the Debye–Hückel equation (Dean 1999) (for 20 °C); $C(\text{SO}_3^{2-})$ is the brutto concentration of all sulfite forms in the solution, M .

Determination of potentiometric selectivity coefficients ($\lg K^{\text{Pot}}$) was performed by the separate solutions method in the equal potential variant; all the other characteristics have been determined according to recommendations in Nikol'skii and Materova 1980 and Kamman (1980).

Only freshly boiled distilled water was used while working with carbonate, sulfite and thiosulfate electrodes. The potential of the electrochemical cell was measured with I-160.1MP ion meter at 22 ± 1 °C. The silver chloride electrode EVL-1M3.1 was used as a reference electrode, and pH was determined with the glass electrode ESL-43-07SR, chlorides were determined by precipitation titration with the silver electrode.

Results and discussion

140 membrane compositions for sulfite, molybdate, tungstate, hydrogen phosphate, hydrogen carbonate, thiosulfate, and sulfate ISEs have been studied. Electrode functions of the best ISEs (with optimized compositions, see Table 1) developed are given in Figs. 2, 3. The main criteria for the optimization of membrane composition are selectivity and detection limit.

It is evident from Figs. 2, 3 and Table 2 that all ISEs have quite low LDL (M); high selectivities ($\lg K^{\text{Pot}}$); near-theoretical electrode function slope (S , mV); and that within certain pH range their potential is not pH-dependent. The lifetime for the thiosulfate, sulfite, hydrogen phosphate, molybdate, tungstate ISEs are 10 days, for carbonate ISE is 45 days, sulfate ISE is 20 days. During this time, the analytical characteristics of the ISE do not change more than 95% from the initial values.

On the example of carbonate ISE, the effect of the QAS exchange center steric accessibility upon lower detection limits (LDLs) and potentiometric selectivities has been demonstrated (Table 3). Regularities established are also true for the other ISEs.

Optimized compositions for ISE membranes are presented in Table 1, their analytical characteristics—in Table 2.

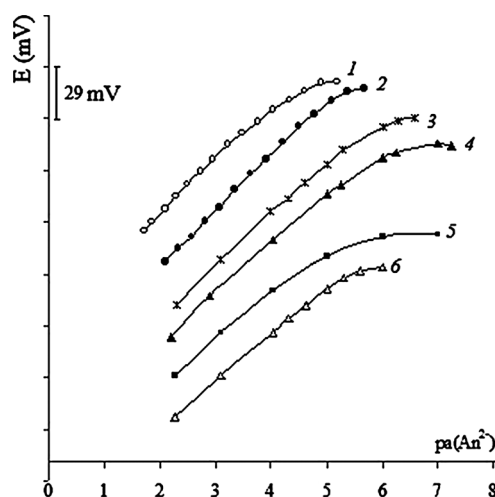
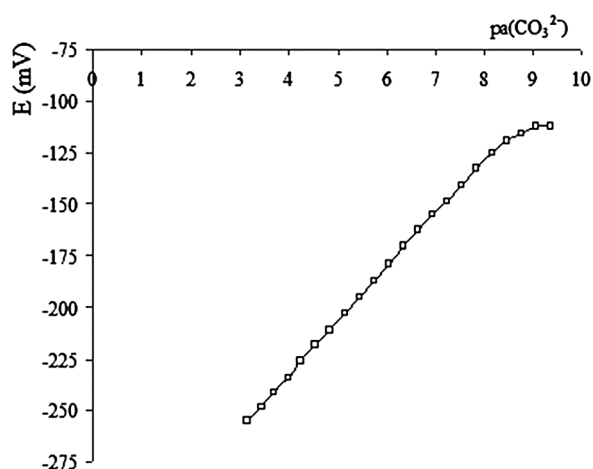
LDLs and $\lg K^{\text{Pot}}$ both for carbonate ISE and for the other ISEs decrease as follows: TNODA > TB > TE > TM > BHPBTM > (oxyethyl)_nTM (Table 3).

The results expressing the effect of QAS exchange center steric accessibility, from TM to (oxyethyl)_nTM, upon total $\lg K^{\text{Pot}}$ to interfering sulfate, chloride and nitrate ions for sulfite, thiosulfate and hydrogen phosphate ISEs (for molybdate ISEs, also to interfering bromide, tungstate and oxalate ions), are represented in Fig. 4.

It should be noted that for tungstate ISEs, the total effect of replacing TM with BHPBTM upon $\lg K^{\text{Pot}}$ is near zero for membranes containing TFABAHE, and in absence of TFABAHE it shows up only for interfering chloride (1 order) and nitrates (1.6 orders).

Table 1 Optimized compositions for ISE membranes

ISEs	QAS	Plasticizer	Neutral carrier
SO ₄ ²⁻	(oxyethyl) ₃ TM, 5% w/w.	1-BN, 42% w/w.	TFABAHE, 20% w/w.
SO ₃ ²⁻	(oxyethyl) ₂ TM, 5% w/w.	DBP, 42% w/w.	TFABAHE, 20% w/w.
S ₂ O ₃ ²⁻	(oxyethyl) ₄ TM, 5% w/w.	DBP, 42% w/w.	TFABAHE, 20% w/w.
WO ₄ ²⁻	BHPBTM, 5% w/w.	DBP, 42% w/w.	TFABAHE, 20% w/w.
	TM, 5% w/w.	DBP, 42% w/w.	TFABAHE, 20% w/w.
MoO ₄ ²⁻	(oxyethyl) ₄ TM, 5% w/w.	DBP, 42% w/w.	TFABAHE, 20% w/w.
CO ₃ ²⁻	1—(oxyethyl) ₃ TM, 5% w/w.	<i>o</i> -DNPE, 52% w/w.	TFABAHE, 10% w/w.
	2—BHPBTM, 2% w/w.	<i>o</i> -DNPE, 55% w/w.	TFABAHE, 10% w/w.
HPO ₄ ²⁻	1—(oxyethyl) ₃ TM, 5% w/w.	DBP, 42% w/w.	TFABAHE, 20% w/w.
	2—(oxyethyl) ₃ TM, 5% w/w.	<i>o</i> -DNPE, 42% w/w.	TFABAHE, 20% w/w.

**Fig. 2** Electrode functions of ISEs with optimized compositions (see Table 1): 1–thiosulfate, 2–sulfite, 3–hydrogen phosphate, 4–sulfate, 5–molybdate, 6–tungstate**Fig. 3** The electrode function of the carbonate ISE based on BHPBTM (2% w/w.), TFABAHE, 10% w/w. and *o*-DNPE (55% w/w.)

For all ISEs, switching from (oxyethyl)₂TM to (oxyethyl)₄TM does not cause any effect upon $\lg K^{\text{Pot}}$ greater than 0.5 order, for any membrane composition.

Replacing TNODA with (oxyethyl)₄TM improves LDLs generally by 1–2 orders; although for sulfite and thiosulfate ISEs the effect is smaller (0.3–0.95 orders).

Figure 5 represents in detail results on the effect of QAS exchange center steric accessibility, from TM to (oxyethyl)₄TM, upon $\lg K^{\text{Pot}}$ for sulfate ISEs.

The effects observed, caused by the influence of the exchange center steric accessibility, on the qualitative level can be interpreted in terms of ion association constant change: upon the model where QAS exists in the form of ionic triples with double-charged anions, not forming more complex aggregates, ion association constants k_{as} are described by Eigen–Denison–Ramsey–Fuoss equation (Nazarov et al. 2011):

$$\lg k_{\text{as}} = -2.6 + 243 \frac{|z^+ a^+ c^-|}{\epsilon a} + 31 g a, \quad (3)$$

where z^+, z^- are charges of the anion and QAS cation being associated; ϵ is the dielectric constant of the solvent; a is the closest approach parameter for cations and anions being associated, Å.

According to Rakhman'ko et al. (1991), in close ion pairs, where no solvent molecules are present between the associated ions, for QAS cations and anions a parameter is about 4–7 Å. Hence, with solvents with low or average ϵ (DBP ($\epsilon = 6.43$), BEHD or 1-BN ($\epsilon = 4 \div 4.99$)) (Lomako et al. 2006), the second member of Eigen–Denison–Ramsey–Fuoss equation makes the main contribution in k_{as} value.

In the first approximation, a parameter is an additive function of the anion and cation radii. It is evident that the effect of QAS exchange center steric accessibility upon association constants should depend upon the size of ions being associated. Clearly, the improvement of steric access should lead to greater ion association constant increase for smaller anions ($r(\text{HCO}_3^-) = 1.56 \text{ \AA}$, $r(\text{CO}_3^{2-}) = 1.78 \text{ \AA}$,

Table 2 Main characteristics of ISEs developed

ISES	pH range	S, mV (n = 5)	LDL, M (n = 5)	$\lg K^{\text{pot}}$ (n = 5)											
				SCN ⁻	C ₂ O ₄ ²⁻	Cl ⁻	Br ⁻	NO ₃ ⁻	SO ₄ ²⁻	WO ₄ ²⁻	MoO ₄ ²⁻	HPO ₄ ²⁻			
SO ₄ ²⁻	3–6	28.3 ± 0.4	(7.0 ± 0.5) × 10 ⁻⁷	0.9 ± 0.1 ^b	-0.25 ± 0.05 ^b	-2.2 ± 0.3	-1.8 ± 0.3	-0.15 ± 0.05							
SO ₃ ²⁻	7.5 ± 0.1 ^a	29.0 ± 0.4	(6.3 ± 0.5) × 10 ⁻⁶			-0.5 ± 0.1		2.8 ± 0.4	-0.9 ± 0.1						
S ₂ O ₃ ²⁻	4.5–5.5	26.6 ± 0.3	(1.6 ± 0.3) × 10 ⁻⁵			-1.25 ± 0.15		0.5 ± 0.1	-1.2 ± 0.2						
WO ₄ ²⁻	10.0 ± 0.2 ^a	24.3 ± 0.2	(4.6 ± 0.4) × 10 ⁻⁶			-0.8 ± 0.1		1.6 ± 0.2	-0.4 ± 0.1				-0.5 ± 0.1		
	10.0 ± 0.2 ^a	25.8 ± 0.3	(4.9 ± 0.3) × 10 ⁻⁶			-0.7 ± 0.1		1.9 ± 0.3	-0.4 ± 0.1				-0.4 ± 0.1		
MoO ₄ ²⁻	10.0 ± 0.2 ^a	24.0 ± 0.2	(2.5 ± 0.4) × 10 ⁻⁶			-0.5 ± 0.1		0.7 ± 0.1	-0.7 ± 0.1				-0.8 ± 0.1		
CO ₃ ²⁻	8.0 ± 0.1 ^a	32.3 ± 0.5	(1.9 ± 0.7) × 10 ⁻⁹	0.7 ± 0.1	-2.6 ± 0.3	-4.3 ± 0.4	-3.1 ± 0.3	-0.9 ± 0.1	-3.8 ± 0.3						
	8.0 ± 0.1 ^a	25.8 ± 0.4	(2.2 ± 0.8) × 10 ⁻⁹	0.8 ± 0.1	-2.5 ± 0.3	-4.2 ± 0.4	-3.2 ± 0.4	-0.5 ± 0.1	-3.7 ± 0.3						
HPO ₄ ²⁻	8–11	29.1 ± 0.3	(5.0 ± 0.5) × 10 ⁻⁷			-2.3 ± 0.3		0.4 ± 0.1	-0.9 ± 0.1						
	8–11	27.3 ± 0.3	(5.0 ± 0.5) × 10 ⁻⁷			-2.6 ± 0.3		0.10 ± 0.05	-1.1 ± 0.1						

^a The molar fraction of HCO₃⁻, WO₄²⁻ and MoO₄²⁻ ions is 100%. For SO₃²⁻, molar fractions range from 67 to 86%

^b For membranes plasticized with DBP

Table 3 The effect of QAS nature upon analytical characteristics of carbonate ISEs

QAS 5% w/w.	LDL, M (n = 4)	S, mV (n = 4)	$\lg K^{\text{pot}}$ (CO ₃ ²⁻ , j) (n = 4)									
			SO ₄ ²⁻	Cl ⁻	HPO ₄ ²⁻	Br ⁻	C ₂ O ₄ ²⁻	NO ₃ ⁻	SCN ⁻			
The neutral carrier 10% w/w. Plasticizer is DBP												
TNODA	(4.6 ± 0.6) × 10 ⁻⁸	26.7 ± 0.3	-2.7 ± 0.3	-3.2 ± 0.4	-0.9 ± 0.2	-2.0 ± 0.3	-1.5 ± 0.2	1.0 ± 0.2	4.0 ± 0.5			
TB	(4.6 ± 0.7) × 10 ⁻⁸	26.5 ± 0.4	-2.7 ± 0.3	-3.2 ± 0.4	-0.9 ± 0.1	-2.0 ± 0.3	-1.5 ± 0.2	1.0 ± 0.2	4.0 ± 0.5			
TE	(1 ± 0.5) × 10 ⁻⁸	28.2 ± 0.4	-2.9 ± 0.3	-3.4 ± 0.4	-1.1 ± 0.2	-2.3 ± 0.4	-1.7 ± 0.2	0.7 ± 0.1	3.2 ± 0.3			
TM	(4.1 ± 0.6) × 10 ⁻⁹	31.5 ± 0.5	-3.0 ± 0.4	-3.6 ± 0.5	-1.2 ± 0.2	-2.5 ± 0.4	-1.9 ± 0.3	0.4 ± 0.1	2.1 ± 0.2			
BHPBTM	(2.2 ± 0.7) × 10 ⁻⁹	28.6 ± 0.3	-3.1 ± 0.4	-3.7 ± 0.5	-1.3 ± 0.2	-2.6 ± 0.4	-2.0 ± 0.3	0.0	1.5 ± 0.2			
(oxyethyl) ₂ TM	(1.0 ± 0.7) × 10 ⁻⁹	33.8 ± 0.5	-3.3 ± 0.4	-3.9 ± 0.5	-1.5 ± 0.2	-2.8 ± 0.5	-2.2 ± 0.3	-0.5 ± 0.1	1.1 ± 0.1			
(oxyethyl) ₃ TM	(1.0 ± 0.7) × 10 ⁻⁹	32.8 ± 0.4	-3.3 ± 0.5	-4.0 ± 0.5	-1.6 ± 0.3	-2.8 ± 0.5	-2.3 ± 0.4	-0.6 ± 0.1	1.0 ± 0.1			
(oxyethyl) ₄ TM	(1.0 ± 0.6) × 10 ⁻⁹	33.2 ± 0.5	-3.3 ± 0.5	-4.0 ± 0.5	-1.6 ± 0.3	-3.0 ± 0.5	-2.3 ± 0.4	-0.8 ± 0.2	0.85 ± 0.15			

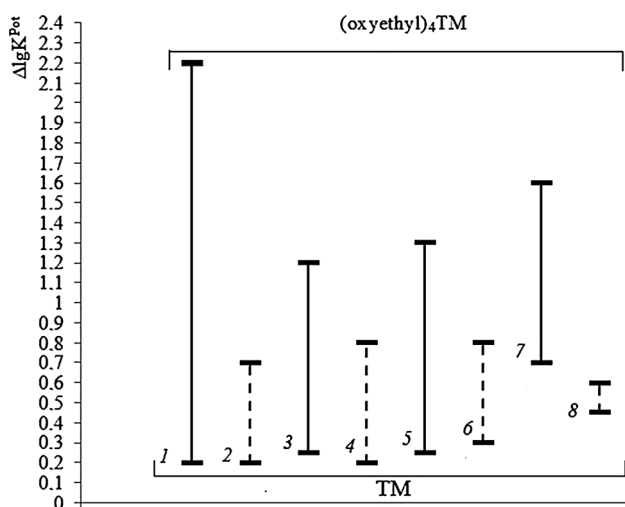


Fig. 4 The total effect of $\lg K^{\text{Pot}}$ change due to replacing TM with $(\text{oxyethyl})_n\text{TM}$ for ISEs: 1–molybdate (without TFABAHE), 2–molybdate (with TFABAHE), 3–sulfite (without TFABAHE), 4–sulfite (with TFABAHE), 5–hydrogen phosphate (without TFABAHE), 6–hydrogen phosphate (with TFABAHE), 7–thiosulfate (without TFABAHE), 8–thiosulfate (with TFABAHE)

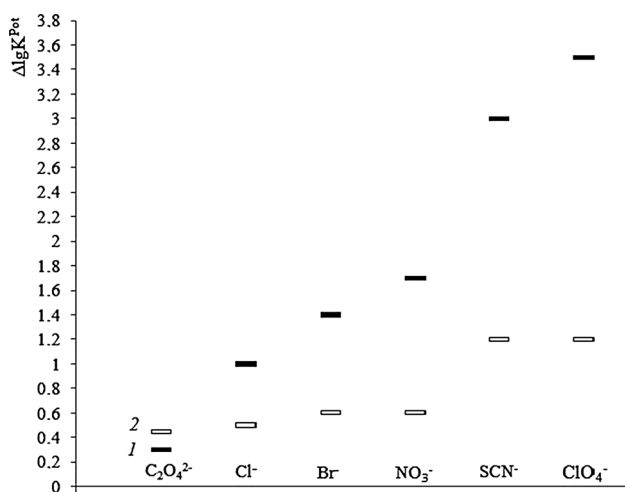


Fig. 5 Total effect of $\lg K^{\text{Pot}}$ change from TM to $(\text{oxyethyl})_4\text{TM}$ for ISEs: 1–sulfate (filled rectangle without TFABAHE), 2–sulfate (open rectangle with TFABAHE)

$r(\text{SO}_4^{2-}) = 2.58 \text{ \AA}$, $r(\text{Cl}^-) = 1.81 \text{ \AA}$, $r(\text{Br}^-) = 1.88 \text{ \AA}$, $r(\text{NO}_3^-) = 1.79 \text{ \AA}$, $r(\text{SCN}^-) = 2.13 \text{ \AA}$ (Jenkins and Thakur 1979). When single-charged anions are substituted for double-charged ones, the drop in the closest approach parameter should considerably increase first association constant of double-charged anion and QAS cation. The removal of steric hindrance for approach of the ion associate ($\text{QAS}^+ \dots \text{An}^{2-}$) to the second QAS cation should be accompanied by increase of the second association constant.

Obviously, the greatest improvement of selectivity to double-charged anions should be achieved in presence of

large single-charged anions, because their association constants are not much dependent on the QAS cation exchange center steric accessibility. Hence, for carbonate and sulfate ISEs, the greatest selectivity improvement toward target ions is attained in relation to bulky single-charged anion such as thiocyanate, while the smallest improvement, for all ISEs developed—in relation to chloride ions. The revealed trend of selectivity improvement remains also in presence of such neutral carrier as TFABAHE.

It has been established that TFABAHE concentration affects both selectivity and the LDL. Increasing TFABAHE proportion in the membrane expectedly improves carbonate ISE selectivity to target ions (Table 4) as compared to the interfering ones, and the effect magnitude depends upon their basicity that determines their affinity to TFABAHE.

Table 4 shows that, for practical purposes, 10% w/w of TFABAHE in the carbonate ISE membrane is enough, because further increases do not significantly improve either selectivity or LDL. However, at 15–20% w/w of TFABAHE, the slope of electrode function shows significant deviations from the theoretical value caused by the appearing mixed response both to carbonate and to hydrogen carbonate ions.

For the rest of ISEs, TFABAHE content in membranes was 20% w/w, because it has been shown in Egorov et al. (2006) on the example of sulfate ISEs, that high selectivity to target ions can be attained only when the neutral carrier is in considerable excess to QAS. The reason of it is that carbonate ions form a very strong complex with TFABAHE (Nazarov et al. 2011), compared to other hydrophilic ions.

It should be noted that introduction of the neutral carrier levels both selectivity improvement and LDL decrease effects, that can be explained by solvate formation between anions and TFABAHE diminishing the effect of exchanging ion size itself.

For carbonate and hydrogen phosphate ISEs, the plasticizer of choice is o-DNPE, while for sulfite, thiosulfate, tungstate and molybdate ISEs, DBP is preferable. For sulfate ISEs, using 1-BN as a plasticizer improves analytical characteristics. This result is in agreement with the data of Rakhman'ko et al. (1990), where it is reported that the affinity of SO_4^{2-} to QAS increases along with decreasing solvating ability of the solvent. This effect is unexpected because normally exchange constants for hydrophilic ions decrease in inert solvents. The possible reason may be weak solvation of sulfate association sites in QAS structure by 1-bromonaphthalene, caused by their low steric accessibility due to shielding by QAS substituents.

Below, some procedures are given for sulfite determination in dried fruits and for carbonate and sulfate determination in mineral water.

Table 4 The effect of the neutral carrier concentration on the analytical characteristics of carbonate ISEs

TFABAHE, % w/w/QAS:TFABAHE molar ratio	LDL, M ($n = 4$)	S, mV ($n = 4$)	$\lg K^{\text{pot}}(\text{CO}_3^{2-}, j)$ ($n = 4$)										
			SO_4^{2-}	Cl^-	HPO_4^{2-}	Br^-	$\text{C}_2\text{O}_4^{2-}$	NO_3^-	SCN^-				
QAS is TM. Plasticizer is DBP													
0	$(1 \pm 0.4) \times 10^{-7}$	28.6 ± 0.4	-0.20 ± 0.05	2.1 ± 0.3	0.0	3.4 ± 0.4	0.5 ± 0.1	4.5 ± 0.4	6.2 ± 0.6				
1 (2:1)	$(5.5 \pm 0.6) \times 10^{-8}$	29.4 ± 0.2	-0.4 ± 0.1	1.8 ± 0.3	0.0	3.0 ± 0.4	0.25 ± 0.05	4.2 ± 0.4	5.7 ± 0.6				
2 (1:1)	$(3.2 \pm 0.5) \times 10^{-8}$	30.7 ± 0.4	-0.8 ± 0.1	1.2 ± 0.2	-0.20 ± 0.05	1.5 ± 0.3	-0.30 ± 0.05	3.5 ± 0.4	4.8 ± 0.4				
5 (1:2)	$(1.0 \pm 0.6) \times 10^{-8}$	31.3 ± 0.3	-1.5 ± 0.2	-0.20 ± 0.05	-0.4 ± 0.1	0.30 ± 0.05	-0.9 ± 0.1	2.6 ± 0.3	4.0 ± 0.4				
7.5 (1:3)	$(6.0 \pm 0.7) \times 10^{-9}$	31.2 ± 0.3	-2.2 ± 0.3	-1.6 ± 0.2	-0.8 ± 0.1	-1.5 ± 0.2	-1.5 ± 0.2	1.3 ± 0.2	2.8 ± 0.3				
10 (1:4)	$(4.1 \pm 0.6) \times 10^{-9}$	31.5 ± 0.4	-3.0 ± 0.4	-3.6 ± 0.4	-1.2 ± 0.2	-2.5 ± 0.3	-1.9 ± 0.2	0.4 ± 0.1	2.1 ± 0.3				
15 (1:6)	$(1.9 \pm 0.7) \times 10^{-9}$	35.7 ± 0.4	-3.4 ± 0.4	-3.9 ± 0.4	-1.7 ± 0.3	-2.9 ± 0.3	-2.1 ± 0.3	0.0	1.5 ± 0.2				
20 (1:8)	$(1 \pm 0.3) \times 10^{-9}$	35.0 ± 0.6	-3.8 ± 0.4	-4.1 ± 0.5	-2.0 ± 0.3	-3.2 ± 0.3	-2.3 ± 0.3	-0.20 ± 0.05	1.1 ± 0.2				

Procedure for determination of hydrogen carbonate and sulfate ions in mineral water. Four carbonate ISEs were used for analyses: N⁰1—TM 5% w/w., TFABAHE 10% w/w., DBP; N⁰2—(oxyethyl)₃TM 5% w/w., TFABAHE 10% w/w., *o*-DNPE; N⁰3—TM 5% w/w., TFABAHE 10% w/w., *o*-DNPE; N⁰4—BHPBTM 2% w/w., TFABAHE 10% w/w., *o*-NDPE. Sulfate determination was performed with the following ISEs: N⁰1—TM 5% w/w., TFABAHE 20% w/w., 1-BN; N⁰2—(oxyethyl)₃TM 5% w/w., TFABAHE 20% w/w., 1-BN.

Sulfate and hydrogen carbonate contents were determined by calibrating plot and limiting solution methods. In the calibrating plot method, 25.0-mL aliquots of mineral water were buffered to pH 8.15 ± 0.05 . The carbonate electrode potentials were then measured, CO_3^{2-} concentration found by calibrating plot and recalculated into hydrogen carbonate concentration using the formula:

$$[\text{HCO}_3^-] = \frac{[\text{CO}_3^{2-}] \cdot [\text{H}^+]}{K_2} \quad (4)$$

In the limiting solution method, two standard solutions were potentiometered, with hydrogen carbonate or sulfate ion concentration long-chain (C_1) or lower (C_2) than their content in the mineral water, along with the sample solution (C_x). The calculations were done according to the formula:

$$1gC_x = \frac{E_x - E_1}{E_1 - E_2} \cdot (1gC_2 - 1gC_1) + 1gC_1 \quad (5)$$

Acid–base potentiometric titration of mineral water samples with 1×10^{-2} M HCl (*Frost*) or with 0.1 M HCl (*Borzhome*) was used as a reference method. Obtained ($n = 4$): for *Frost*, 0.26 ± 0.02 g L⁻¹ HCO_3^- ($S_r = 6.9\%$, label, 0.2–0.6 g L⁻¹), for *Borzhome*, 4.08 ± 0.15 g L⁻¹ HCO_3^- ($S_r = 3.0\%$, label, 3.5–5.0 g L⁻¹). Chloride ions were determined by the potentiometric precipitation titration with 1×10^{-2} M silver nitrate solution. Obtained ($n = 4$): for *Frost*, 0.64 ± 0.04 g L⁻¹ Cl^- ($S_r = 6.2\%$, label, 0.4–0.8 g L⁻¹), for *Borzhome*, 0.42 ± 0.03 g L⁻¹ Cl^- ($S_r = 7.7\%$, label, 0.25–0.5 g L⁻¹).

For sulfate ion determination in *Frost* mineral water, pH was buffered to 3.20 ± 0.05 , to remove interference from hydrogen carbonates; to destroy magnesium and calcium sulfate complexes and to reduce the interference of chlorides, samples were diluted to SO_4^{2-} concentration approximately 5×10^{-5} M.

For reference, gravimetric sulfate determination in the form of BaSO_4 was used, after concentrating the samples 25 times by evaporating. Obtained ($n = 4$): 0.082 ± 0.001 g L⁻¹ SO_4^{2-} ($S_r = 1.3\%$). No sulfate determination was performed in *Borzhome* mineral water, because the nominal concentration claimed by the producer is too low, and concentrating samples is not appropriate

Table 5 Results of hydrogen carbonate and sulfate potentiometric determinations with ISEs in mineral waters

CO ₃ ²⁻ ISEs	By the calibration plot (n = 8)		Limiting solution method (n = 5)		By the calibration plot (n = 8)		Limiting solution method (n = 5)	
	HCO ₃ ⁻ , g L ⁻¹	S _r , %	HCO ₃ ⁻ , g L ⁻¹	S _r , %	HCO ₃ ⁻ , g L ⁻¹	S _r , %	HCO ₃ ⁻ , g L ⁻¹	S _r , %
	<i>Frost</i> (label, 0.2–0.6 g L ⁻¹ HCO ₃ ⁻)				<i>Borzhomi</i> (label, 3.5–5.0 g L ⁻¹ HCO ₃ ⁻)			
1	0.28 ± 0.02	6.4	0.30 ± 0.03	8.7	4.31 ± 0.23	5.2	4.20 ± 0.20	4.5
2	0.26 ± 0.03	10.9	0.29 ± 0.03	7.4	4.54 ± 0.28	6.4	4.35 ± 0.25	5.8
3	0.31 ± 0.04	11.8	0.30 ± 0.04	11.6	4.24 ± 0.15	3.8	4.11 ± 0.16	4.1
4	0.29 ± 0.03	9.5	0.28 ± 0.03	10.8	3.93 ± 0.26	5.7	4.03 ± 0.11	3.4
SO ₄ ²⁻ ISEs	<i>Frost</i> (label, 0.01–0.1 g L ⁻¹ SO ₄ ²⁻)				<i>Borzhomi</i> (label, < 10 mg L ⁻¹ SO ₄ ²⁻)			
1	0.074 ± 0.010	14.2	0.079 ± 0.012	14.0	–	–	–	–
2	0.089 ± 0.013	16.4	0.081 ± 0.011	13.4	–	–	–	–

Table 6 Results of potentiometric and iodometric determination of sulfites in dried fruits

SO ₃ ²⁻ ISEs	Apricots				Raisins			
	By the calibration plot (n = 7)		Limiting solution method (n = 6)		By the calibration plot (n = 7)		Limiting solution method (n = 6)	
	SO ₃ ²⁻ , mg kg ⁻¹	S _r , %	SO ₃ ²⁻ , mg kg ⁻¹	S _r , %	SO ₃ ²⁻ , mg kg ⁻¹	S _r , %	SO ₃ ²⁻ , mg kg ⁻¹	S _r , %
1	1280 ± 120	8.7	1130 ± 160	10.8	1600 ± 120	6.8	1690 ± 200	11.3
2	1520 ± 180	7.2	1380 ± 140	8.1	1520 ± 160	8.3	1610 ± 170	9.2
Iodometry			1200 ± 50	3.6	Iodometry		1880 ± 70	2.9

here, due to increased concentration of interfering chloride ions. The determination results are given in Table 5.

There is an agreement between the results of different methods providing the evidence of their correctness and of good selectivity of ISEs suggested. It should be noted that sulfate determination in *Frost* mineral water is characterized by high S_r values caused by stronger chloride interference upon sulfate ISEs, as compared to carbonate ones.

Procedure for sulfite determination in dried fruits (apricots, raisins). Samples of dried fruits (100.0 ± 0.1 g) were soaked in distilled water for 40 min under occasional stirring. Obtained water extracts were filtered, filtrates transferred into 250.0-mL volumetric flasks. Residual fruits were additionally washed with two portions of distilled water, washings filtered as well and the obtained extracts combined. Then, reverse iodometric determination of sulfites was done according to the procedure given in Alekseev (1972).

For potentiometric sulfite determination, 10.0-mL aliquots of prepared water extracts were taken, transferred to 100.0-mL volumetric flasks and diluted to volume with 1 × 10⁻² M ascorbic acid neutralized with ammonia to pH 7.5 ± 0.1. Sulfites were determined by calibrating plot and limiting solution methods (Table 6). For potentiometric

determination, electrodes based on TM (1) and BHPBTM (2) with 20% w/w of TFABAHE (DBP as a plasticizer) were used.

According to Buldakov (2003), the threshold limit value of sulfites in dry fruits (depending upon the kind) is 500–2000 mg kg⁻¹.

The procedures proposed can be recommended for express control of sulfites, hydrogen carbonates and sulfates in water and food objects in practice of industrial and food laboratories. Their main advantages are simplicity of execution and little or no need for use of extra reagents or expensive equipment.

Conclusions

The influence of long-chain quaternary ammonium salts exchange center steric accessibility and the neutral carrier (4-trifluoroacetyl benzoic acid heptyl ester) on the analytical characteristics of ion-selective electrodes reversible to MoO₄²⁻, WO₄²⁻, SO₄²⁻, HPO₄²⁻, SO₃²⁻, CO₃²⁻, S₂O₃²⁻ ions, has been studied. The net effect of the access improvement upon selectivity coefficient depends upon the nature of the interfering ion, reaching the greatest values

for hydrophobic thiocyanate ions (6–8 orders, in carbonate- and sulfate-selective electrodes) and 3.4–5.7 orders for nitrate ions, while the smallest effect is observed for hydrophilic sulfate, chloride and oxalate ions. Lower detection limit improvements caused by replacing the least accessible salt by the most accessible one, are generally about 1–2 orders, and for sulfite or thiosulfate electrodes no more than 0.3–0.95 orders. Analytical procedures for determination of sulfate, sulfite and carbonate ions in real objects (mineral water, dried fruits) have been proposed.

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