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Modification and validation of the pyromellitic acid electrolyte for the capillary electrophoretic determination of anions ☆

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Abstract

For the determination of inorganic and organic anions, the pyromellitic acid (PMA) electrolyte is widely used. The pH adjustment of the self-prepared electrolyte was very challenging to satisfy the pH of specification of pH 7.8±0.1. A modification was proposed to provide a more simple electrolyte by buffering the PMA electrolyte with triethanolamine (TEA) only instead of adjusting the pH by NaOH and TEA. Thus, the proposed electrolyte consisted of 2.25 mmol l^{-1} PMA, 0.75 mmol l^{-1} hexamethonium hydroxide and 12 mmol l^{-1} TEA. The performance of the PMA electrolyte buffered by TEA only was compared to a commercial available PMA and statistically validated in accordance with the methodology of Taguchi. No statistically significant difference could be found for both electrolytes assessing the performance and detection limits of hydrodynamic, stacking and electrokinetic injection with transient isotachophoretic preconcentration as well as repeatability of migration times, peak resolutions and peak symmetries.

Keywords: Background electrolyte composition; Validation; Inorganic anions; Organic anions; Pyromellitic acid; Hexamethonium hydroxide

1. Introduction

Capillary electrophoresis (CE) is widely used for the determination of inorganic and organic anions in different matrices. Initially, the separation of fast migrating anions was dominated by the chromate electrolyte but because of the toxicity of chromate this electrolyte was gradually replaced by the pyromellitic acid (PMA) electrolyte. While the original composition of the chromate electrolyte was modified and adjusted in many different ways since its first publication in 1990 [1], the PMA electrolyte is in use with virtually no changes since its introduction in 1993 [2]. Originally, the chromate electrolyte consists of 5 mmol l^{-1} sodium chromate and 0.5 mmol l^{-1} tetradecyltrimethylammonium bromide patented as OFM-Anion-BT by Waters [3] and is adjusted to pH 8.0. Since then the electrolyte has

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experienced a lot of variations, e.g., in the concentration of chromate [4,5], in type and concentration of the endoelectroosmotic flow (EOF) modifier [4,6–13], additives, e.g., organic solvents [4,8,9,11,13–15], pH and chemicals used for pH adjustment [5,8,12,13,16–18]. Therefore, there is no widely accepted composition of the chromate electrolyte. In contrast, the PMA electrolyte can be regarded as almost standardized containing 2.25 mmol^{-1} PMA, 6.5 mmol^{-1} NaOH, 1.6 mmol^{-1} triethanolamine (TEA) and 0.75 mmol^{-1} hexamethonium hydroxide (HMOH) at pH 7.8±0.1. In the literature, the electrolyte composition was used without any modification [2,19–23]. Nevertheless, some changes to the PMA electrolyte were suggested considering the concentration of PMA, type and concentration of EOF modifier [24–26].

In our laboratory the standard PMA electrolyte is successfully used for the ultra trace analytical determination of anionic contaminants, i.e., bromide, chloride, sulfate, nitrite, nitrate, oxalate, fluoride, formate, and phosphate, on silicon wafer surfaces, process media and cleanroom air on a daily routine. For task force analyses, the analyte spectrum can be extended by some inorganic anions, e.g., dithionate, thiosulfate, chromate, diphosphate, tetrafluoroborate, fluorophosphate, arsenate, and organic anions, e.g., citrate, malonate, maleate, tartrate, succinate, glutarate [27–29]. In reducing analytical costs, the electrolyte is prepared the laboratory but pH adjustment was found to be challenging because of the presence of NaOH. Considering the approach of the chromate electrolyte adjusting the pH by using a buffer [12,17], the question arose why the pH of the PMA electrolyte was adjusted by NaOH and TEA. We present here a systematic investigation on, and validation of, the buffering of the PMA electrolyte in a chemometric approach.

2. Experimental

2.1. Apparatus

All experiments were carried out using an Agilent Technologies ^{3D}CE system (Agilent Technologies, Waldbronn, Germany) at a constant temperature of 20 °C. Fused-silica capillaries were obtained from Polymicro Technologies (Phoenix, AZ, USA). For the determination of anions, the capillaries were of 48.5 cm×50 μm I.D. Indirect UV detection was carried out at 350 nm with a bandwidth of 60 nm and a reference wavelength of 245 nm with a bandwidth of 10 nm. A separation voltage of −30 kV was applied.

To quantify the amount of the cationic compounds in the laboratory-made and commercial PMA electrolytes a capillary of 64.5 cm×50 μm I.D. was used (Polymicro Technologies). Signal wavelength was set to 240 nm with a bandwidth of 10 nm and a reference wavelength of 210 nm with a bandwidth of 10 nm using a diode array detector for indirect UV detection was used. Separation was carried out at +30 kV.

The pH was measured by a 340 pH meter from Mettler Toledo (Giessen, Germany) with automatic temperature compensation and automatic endpoint detection equipped with an InLab electrode of type 415 (Mettler Toledo) in an air-conditioned laboratory at 20±1 °C. The instrument was calibrated daily using a traceable commercial available buffer solution at pH 4.00 (citrate–hydrochloric acid), pH 7.00 (phosphate) and pH 10.00 (boric acid–potassium chloride–NaOH) from Merck (Darmstadt, Germany).

2.2. Reagents

Chemicals were purchased from various suppliers and were of analytical grade or better. The sodium salts of bromide, chloride, sulfate, nitrite, nitrate, oxalate, formate, phosphate, 1 mol l^{-1} NaOH, tris(hydroxymethyl)aminomethane (Tris) and pyromellitic acid were purchased from Merck, sodium fluoride and tetrabutylammonium acetate from Aldrich (Sigma–Aldrich, Deisendorf, Germany). Lithium perchlorate, triethanolamine, imidazol, 18-crown-6 ether, acetic acid, triethanolamine hydrochloride, propionic acid, hexamethonium bromide and hexamethonium hydroxide solution of 100 mmol l^{-1} were obtained from Fluka (Sigma–Aldrich). Commercially available PMA electrolytes were obtained from Agilent Technologies. The ultra pure water (UPW) fulfilled the requirements of the ASTM D-5127-99 Standard Guide for Ultra Pure Water Used in the Electronics and Semiconductor Industry,

Type E-1.2 [30], i.e., cations in the range of 5 pg ml^{-1} and inorganic anions in the range of 20 pg ml^{-1}.

2.3. Preparation of electrolytes and stock solutions

A 50-mmol l^{-1} HMOH solution was prepared in the laboratory by ion exchange of the bromide salt using the ion-exchange resin AG 1-X8 (dry mesh size 20–50) in the hydroxide form (Bio-Rad, Hercules, CA, USA) according to Ref. [31]. Considering the equivalent molarity of the modifier, the resin was added to the modifier solution in 10% excess, stirred overnight and filtered (0.2 μm, polyamide). An aliquot of the filtrate was acidified with nitric acid and 5 ml of a solution of 5% silver nitrate was added. The ion exchange was considered complete when no opalescence or precipitation occurred, otherwise the process was repeated by adding fresh resin to the filtrate.

Electrolytes and standard stock solutions of each individual analyte were prepared in a cleanroom of Class 7 by the specification of ISO 14644-1 [32]. The standard reference solutions were daily diluted from the stock solutions in a cleanroom of Class 4 (ISO 14644-1). Stock solutions of 25 mmol l^{-1} for anions were made from the corresponding sodium salts and for cations from the corresponding nitrate or halide salts, respectively.

The self-prepared pyromellitic acid electrolytes consisted of 2.25 mmol l^{-1} PMA, 6.5 mmol l^{-1} NaOH, 0.75 mmol l^{-1} HMOH, 1.1 mmol l^{-1} TEA at pH 7.8; 2.25 mmol l^{-1} PMA, 0.75 mmol l^{-1} HMOH, 9.1 mmol l^{-1} Tris at pH 7.8 and 2.25 mmol l^{-1} PMA, 0.75 mmol l^{-1} HMOH, 12 mmol l^{-1} TEA at pH 7.8.

To determine the real composition of the laboratory-made and commercial PMA electrolytes the cationic compounds in the electrolytes were studied using an imidazole electrolyte consisting of 10 mmol l^{-1} imidazole, 2 mmol l^{-1} 18-crown-6 ether and 16 mmol l^{-1} acetic acid at pH 4.8. Samples were hydrodynamically injected applying 5 kPa for 10 s covering a linear range from 5 to 250 μmol l^{-1}.

All self-prepared electrolytes were filtered (0.2 μm, polyamide, Nalgene, VWR International, Darmstadt, Germany) and degassed in an ultrasonic bath (30 min) prior to use. The commercial PMA electrolyte was used as delivered.

2.4. Capillary conditioning

A new capillary was conditioned at 40 °C for 30 min with 500 mmol l^{-1} NaOH, 10 min with UPW, 30 min with the corresponding the electrolyte by applying 0.1 MPa. A voltage of 30 kV was applied while cooling down to 20 °C. The capillary was then equilibrated under separations by running 10 consecutive analyses. For storage overnight, the capillary was filled with electrolyte, and for long-term storage, the capillary was flushed for 10 min with UPW and 5 min with air.

For the determination of anions, the capillary was pre-conditioned with one capillary volume (0.1 MPa for 0.5 min) of 250 mmol l^{-1} propionic acid and with six capillary volumes (0.1 MPa for 3 min) of electrolyte before each analysis [28] and for the determination of cations, the capillary was only flushed with six capillary volumes (0.1 MPa for 5 min) of electrolyte. For both the determination of anions and cations, the vials containing electrolyte were replenished before each analysis. Capillary rinsing was done out of a separate vial avoiding any cross-contamination and siphoning effects due to different electrolyte levels in the inlet and outlet vials.

2.5. Statistical assessment

In assessing the pyromellitic acid electrolytes, calibration curves were made for hydrodynamic injection, injection with sample stacking and electrokinetic injection with transient isotachophoretic preconcentration of standard mixtures containing bromide, chloride, sulfate, nitrite, nitrate, oxalate, fluoride, formate, and phosphate covering a total concentration range from 0.05 to 100 μmol l^{-1}. Hydrodynamic injection was performed at 2.5 kPa for 10 s with anion standards of blank, 5, 10, 25, 50 and 100 μmol l^{-1}. For sample stacking, first 10 mmol l^{-1} NaOH was injected at 2.5 kPa for 10 s followed by a water dip for 5 s and then the standard was injected at 5 kPa for 95 s [33]. The concentrations were blank, 0.5, 1, 2.5, 5, and 10 μmol l^{-1}. For electrokinetic injection with isotachophoretic preconcen-

tration, 0.25 μmol l^{-1} lithium perchlorate was added to the standard as internal standard and 25 μmol l^{-1} tetrabutylammonium acetate as terminating ion and for normalization of the conductivity of the solution by pipetting 5 μl to 500 μl sample solution. First a plug of 10 mmol l^{-1} NaOH was hydrodynamically introduced at 2.5 kPa for 10 s and a subsequent dip in UPW for 10 s afterwards the standard was injected by applying −10 kV for 10 s [20]. The concentrations were blank, 0.05, 0.1, 0.15, 0.25 and 0.5 μmol l^{-1}. For each injection mode, five repetitions were performed for each concentration. The repeatability of migration times of each anion were estimated as relative standard deviation (RSD) of the different concentrations and injection modes. For the evaluation of peak symmetry and peak resolution of each anion, the highest concentration of each anion was taken considering the injecting mode because the highest concentration showed the greatest deviation from optimum appearance. For a statistical assessment of the calibration curves, the methodology of Taguchi was applied in the dynamic approach and to migration times repeatability, peak symmetries and peak resolutions the static approach was used [34]. In the dynamic approach of Taguchi's method, the investigated concentration ranges were evaluated as a so called ''linear equation'' by an ANOVA (analysis of variance) regarding the four PMA electrolytes as single factors and in the static approach repeatability of migration times was evaluated by a ''smaller the better'' characteristics while for peak symmetries and peak resolutions the ''nominal the best'' characteristics was used [34]. The sensitivities as the slopes of the calibration curves and the variations of systems described as variances of the slopes of each electrolyte for each injection mode were calculated and transformed into a signal-to-noise (S/N) ratio dividing the sensitivity by the variance of the slope. The S/N transformation simplified the evaluation of the electrolytes: the higher the S/N ratio and the higher the sensitivity the better the total performance of the electrolyte for the investigated injection mode. S/N consideration combined with ANOVA calculation allowed a precise evaluation the four electrolytes regarding the different injection modes. All statistical calculations were performed with Statgraphics Plus 5.0 (Statistical Graphics, Rockville, MD, USA).

3. Results and discussion

During the development of methods for the ultra trace analytical determination of anionic contaminants of silicon wafer surfaces, process media and cleanroom air [9,27–29] the PMA electrolyte was considered as optimal. Nevertheless, adjusting the pH to 7.8±0.1 was challenging using the specified concentration of NaOH and TEA, even exact weighing in of the bases could not guarantee the specified pH value. Changing from a laboratory-made HMOH solution to the commercially available HMOH solution did not improve the difficulties.

At first, the concentration of the commercial available HMOH solution was checked. Therefore, the concentration of hexamethonium cation was determined by applying the imidazole electrolyte. Because of its interaction with the capillary wall the standard addition procedure was used. The found concentration of the HMOH solution did not deviate from the concentration specified by the manufacturer. But the concentration of the self-prepared HMOH solution was lower than expected, 36 mmol l^{-1} instead of 50 mmol l^{-1}. Probably, hexamethonium ions were irreversibly bonded to the resin of the ion exchanger by the interaction between the alkyl chains and polymeric materials of the resin. Thus, the cationic composition of the commercial available PMA electrolyte was checked: sodium was found at 6.18 mmol l^{-1}, hexamethonium at 0.58 mmol l^{-1} and triethanolammonium at 1.31 mol l^{-1}. Obviously, this deviation from the original composition was necessary to obtain a pH value within of pH 7.7 to 7.9 according to the certificate of analysis and according to our own measurement.

For this reason the pH of an laboratory-made PMA electrolyte consisting of 2.25 mmol l^{-1} PMA, 0.75 mmol l^{-1} HMOH taken from the commercial available HMOH solution and 6.5 mmol l^{-1} NaOH was newly titrated with TEA. For a pH in the range of pH 7.8±0.1, the concentration of TEA was limited from 0.97 to 1.19 mmol l^{-1} which is clearly lower than specified in the literature [2,19–23]. Thus, the slightest pipetting error resulted in pH outside the aimed range.

Ref. [2] describes the PMA electrolyte for the first time but did not give any reason for a pH adjustment by TEA and NaOH. Buffering by TEA only is

superior to because of the pK_a value of TEA at 7.8 and its buffering range from pH 7.3 to 8.3 [35]. Thus, the electrolyte consisting of 2.25 mmol l^{-1} PMA and 0.75 mmol l^{-1} HMOH was titrated to TEA. For a pH of 7.8±0.1, a concentration of 12.0±1.1 mmol l^{-1} TEA could be added to the electrolyte. A slight inconvenience for electrolyte preparation was the high viscosity of TEA because a stock solution of 1 mol l^{-1} had to be prepared. Thus, Tris was evaluated as a substitute for TEA because of its pK_a value of 8.08 [36] and because as a crystalline solid it can directly be weighted in. An electrolyte consisting of 2.25 mmol l^{-1} PMA and 0.75 mmol l^{-1} HMOH was titrated to Tris and 9.1±0.5 mmol l^{-1} Tris resulted in a pH value of 7.8±0.1.

For the evaluation of the four PMA electrolytes, i.e., commercially available, laboratory-made with 2.25 mmol l^{-1} PMA, 0.75 mmol l^{-1} HMOH, 6.5 mmol l^{-1} NaOH and 1.1 mmol l^{-1} TEA, 2.25 mmol l^{-1} PMA, 0.75 mmol l^{-1} HMOH buffered with 12 mmol l^{-1} TEA and 2.25 mmol l^{-1} PMA, 0.75 mmol l^{-1} HMOH buffered with 9.1 mmol l^{-1} Tris, a statistical validation in accordance to the methodology of Taguchi was applied in the dynamic approach for the calibration curves and for migration times repeatability, peak symmetries and peak resolutions the static approach was used [34] for bromide, chloride, sulfate, nitrite, nitrate, oxalate, fluoride, formate, and phosphate.

From previous investigations the linear range of hydrodynamic injection, sample stacking and electrokinetic injection with transient isotachophoretic preconcentration was know [20,33] covering a concentration range from 0.05 to 100 μmol l^{-1}. Consequently, these ranges were used for the statistical assessment of the four PMA electrolytes. The results of ANOVA, the S/N and sensitivity assessment of the calibration curves as well as migration time reproducibilities, peak symmetries and peak resolutions considering the injection modes and the analytes separately showed no significant differences at a 95% confidence level for the investigated PMA electrolytes. But for the electrolyte, buffered by Tris, sulfate and nitrite co-migrated and, thus, this electrolyte was not further considered. It was assumed that the co-migration was caused by the interaction of Tris and HMOH with sulfate and nitrite because electrolytes buffered with Tris but employing other EOF modifiers did not show this co-migration phenomenon [17,37]. Furthermore, this assumption was supported by experiments using a chromate electrolyte buffered with Tris as described in [17] using HMOH concentration. Only at a HMOH concentration below 0.75 mmol l^{-1} no co-migration occurred. But at lower HMOH concentration the analysis time was prolonged and the peak shapes of phosphate was more skewed (data not shown). For the self-prepared PMA electrolytes buffered by NaOH and TEA, only buffered by TEA and the commercial PMA electrolyte, no significant difference could be revealed regarding their performances. Therefore, Table 1 only summarizes the regression data of the commercial available PMA electrolyte and the self-prepared PMA buffered by TEA only and Fig. 1 depicts the corresponding electropherograms using electrokinetic sample injection because electrokinetic injection was more sensitive to any changes of the electrolyte composition. But as could be seen from Fig. 1 there were no differences in the appearance of the peaks. In Table 1 the data of calibration curves of the different injection modes and investigated anions showed no significant difference. For some anions, the commercial available PMA electrolyte seemed to be favorable and for other anions investigated the PMA electrolyte buffered by TEA only was slightly better. Considering the standard error of the injection modes for each anion the commercial available PMA electrolyte was slightly better for hydrodynamic injection while for sample stacking and electrokinetic injection with transient isotachophoretic preconcentration the PMA electrolyte buffered by TEA only seemed to be more favorable. This slight difference in the electrophoretic behavior could be explained by higher ionic strength of the PMA electrolyte buffered by TEA only: a higher ionic strength is favorable for sample preconcentration during the injection because of the higher drop of the electrical field at the border between sample plug and electrolyte zone.

In Table 2 the repeatability of migration times, peak symmetries and peak resolutions are summarized. For migration time repeatability, the relative standard deviation was calculated from five repetitions of five different concentrations (n=25). Peak symmetry and resolution were calculated from five

Table 1
Calibration data of different injection modes for commercial available PMA electrolyte and self-prepared PMA electrolyte buffered by TEA only

	Commercial electrolyte			TEA buffered electrolyte		
	Slope±SD ($\cdot 10^{-4}$)	Intercept±SD ($\cdot 10^{-4}$)	Standard error ($\cdot 10^{-5}$)	Slope±SD ($\cdot 10^{-4}$)	Intercept±SD ($\cdot 10^{-4}$)	Standard error ($\cdot 10^{-5}$)
Hydrodynamic injection						
Bromide	1.09±0.04	0.99±2.1	5.46	1.13±0.05	3.94±2.6	6.78
Chloride	1.26±0.08	8.39±3.9	9.98	1.21±0.09	2.90±4.9	12.54
Sulfate	2.28±0.08	1.32±4.3	11.04	2.37±0.04	3.36±1.8	4.66
Nitrite	1.10±0.03	2.39±1.3	3.45	1.17±0.01	4.29±6.0	1.56
Nitrate	1.24±0.06	2.20±2.9	7.52	1.26±0.13	7.80±6.6	17.15
Oxalate	2.31±0.01	1.29±6.0	15.40	2.33±0.01	4.38±6.0	15.48
Fluoride	1.48±0.08	3.04±4.1	10.61	1.38±0.01	2.60±7.0	17.98
Formate	1.35±0.04	3.07±2.1	5.52	1.40±0.10	1.76±5.2	13.49
Phosphate	3.01±0.16	6.80±8.0	20.60	2.60±0.10	2.27±5.2	13.53
Injection by sample stacking						
Bromide	18.96±1.1	1.79±5.6	14.43	18.85±1.0	4.02±5.3	13.55
Chloride	19.05±1.6	14.64±8.3	21.49	19.88±1.2	5.00±6.1	15.71
Sulfate	40.89±3.6	4.61±18.6	47.90	41.31±2.6	1.10±13.1	33.84
Nitrite	17.91±1.8	4.57±9.4	24.37	17.32±1.6	8.65±8.4	21.66
Nitrate	21.14±2.2	6.26±11.5	29.79	21.11±0.7	6.99±3.6	9.23
Oxalate	39.28±3.0	8.86±15.4	39.72	38.96±1.2	7.25±6.3	16.36
Fluoride	25.37±2.8	10.77±14.6	37.60	23.24±1.8	10.87±9.2	23.68
Formate	26.39±1.6	14.97±8.1	20.84	23.51±1.2	7.06±6.1	15.79
Phosphate	53.75±2.9	23.97±14.84	38.33	46.83±0.7	2.79±3.7	9.59
Electrokinetic injection with transient isotachophoretic preconcentration						
Bromide	529.17±45.5	19.36±12.0	27.75	506.13±39.8	21.09±10.5	24.29
Chloride	502.67±35.7	60.92±9.4	21.80	473.01±48.26	46.23±12.7	29.44
Sulfate	1186.70±137.7	53.60±36.3	84.04	1101.13±95.8	40.66±25.3	58.45
Nitrite	444.65±47.4	20.17±12.5	28.90	405.46±22.7	45.01±6.0	13.86
Nitrate	486.31±40.6	39.21±10.7	24.76	428.93±31.4	50.78±8.3	19.16
Oxalate	1060.67±119.6	28.09±31.5	72.99	940.75±91.2	29.41±24.05	55.67
Fluoride	343.34±23.73	17.51±6.3	14.48	330.64±17.9	57.86±4.72	10.72
Formate	371.74±29.7	21.34±7.8	18.14	358.99±18.9	50.45±5.0	11.54
Phosphate	592.77±50.0	20.93±13.2	30.72	544.44±35.5	12.79±9.4	21.66

Each calibration curve was obtained at six concentrations with five repetitions. For hydrodynamic injection, 0, 5, 10, 25, 50, 100 μmol l^{-1}, for injection with sample stacking, 0, 0.5, 1, 2.5, 5, 10 μmol l^{-1}, and for electrokinetic injection, 0, 0.05, 0.1, 0.15, 0.25, 0.5 μmol l^{-1} were used.
Standard error of estimation was calculated by:

$$s_{y,x} = \sqrt{\left[\frac{1}{n(n-2)}\right] \cdot \left[n\sum y^2 - \left(\sum y\right)^2 - \frac{\left[n\sum xy - \left(\sum x\right)\left(\sum y\right)\right]^2}{n\sum x^2 - \left(\sum x\right)^2}\right]}$$

repetition of the highest concentration of the corresponding linear ranges of each injection modes assuming that the deviation from optimum behavior was more pronounced. For hydrodynamic and electrokinetic injection, migration time repeatability was better for a PMA electrolyte buffered by TEA only while for sample stacking the commercial PMA showed an better performance for the fast migrating anions. Probably, the commercial PMA electrolyte could better tolerate a longer sample zone during stacking. A long sample zone reduced the dynamic coating of EOF modifier by washing away hexa-

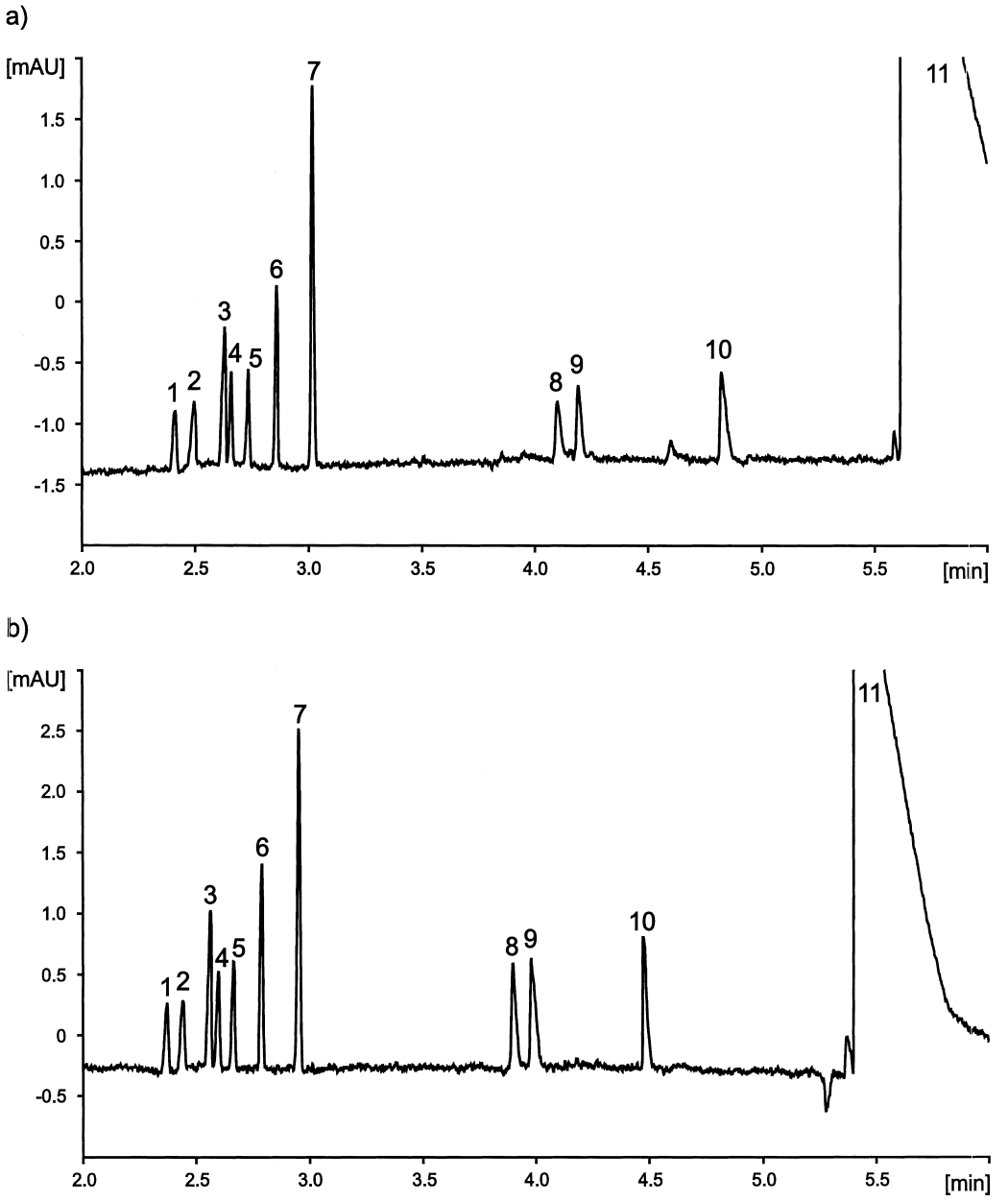

Fig. 1. Electropherograms of a 50 nmol l^{-1} standard of anions obtained with (a) commercial available PMA electrolyte and (b) with PMA electrolyte buffered by TEA only. (1) Bromide, (2) chloride, (3) sulfate, (4) nitrite, (5) nitrate, (6) oxalate, (7) perchlorate (internal standard at a concentration of 250 nmol l^{-1}), (8) fluoride, (9) formate, (10) phosphate, (11) carbonate (from preconcentration procedure using NaOH). For experimental conditions see text.

methonium from the capillary wall which resulted in a higher local EOF towards the cathode [38,39]. In addition the sodium cation was much smaller than the triethanolammonium cation and did not hamper the re-adsorption of hexamethonium at the capillary wall in such an extent as triethanolammonium.

Table 2
Repeatability of migration times, peak symmetry and peak resolution for commercial available PMA electrolyte and self-prepared PMA electrolyte buffered by TEA only regarding the investigated injection mode

	Commercial electrolyte			TEA buffered electrolyte		
	Migration time repeatability	Peak symmetry	Peak resolution	Migration time repeatability	Peak symmetry	Peak resolution
Hydrodynamic injection						
Bromide	0.38	2.80	–	0.31	3.41	–
Chloride	0.35	2.45	3.34	0.32	2.44	3.04
Sulfate	0.56	3.83	5.60	0.44	4.39	5.32
Nitrite	0.42	1.90	1.75	0.35	2.36	1.56
Nitrate	0.42	2.07	3.45	0.30	2.58	3.06
Oxalate	0.57	2.69	6.12	0.38	3.70	6.01
Fluoride	1.11	0.25	41.05	0.39	0.28	40.14
Formate	1.13	0.23	2.40	0.41	0.25	2.51
Phosphate	1.13	0.11	11.13	0.59	0.16	11.99
Injection by sample stacking						
Bromide	0.22	3.87	–	0.43	4.06	–
Chloride	0.23	3.21	2.66	0.46	3.59	2.28
Sulfate	0.14	4.67	4.13	0.58	3.40	3.55
Nitrite	0.18	2.34	0.95	0.54	2.61	1.04
Nitrate	0.28	2.62	2.69	0.49	3.04	2.32
Oxalate	0.25	4.11	4.31	0.52	4.72	4.33
Fluoride	0.95	0.10	26.91	0.62	0.27	27.43
Formate	0.90	0.19	1.66	0.64	0.22	1.78
Phosphate	1.22	0.07	7.24	0.93	0.07	8.59
Electrokinetic injection with transient isotachophoretic preconcentration						
Bromide	0.62	1.60	–	0.21	1.32	–
Chloride	0.69	2.86	2.20	0.26	2.50	1.68
Sulfate	0.79	5.53	3.98	0.46	3.03	3.04
Nitrite	0.76	2.69	0.91	0.40	2.96	0.95
Nitrate	0.73	2.94	3.04	0.28	3.37	2.32
Oxalate	0.79	4.38	5.17	0.39	4.91	4.58
Fluoride	1.13	0.19	29.49	0.31	0.30	29.10
Formate	1.11	0.19	2.00	0.32	0.23	1.96
Phosphate	1.47	0.09	10.74	0.45	0.16	9.75

Regarding peak symmetry and resolution only standards of 100, 10 and 0.05 μmol l^{-1} concentration were taken into account for hydrodynamic injection, sample stacking and electrokinetic injection with transient isotachophoretic preconcentration, respectively.

The detection limits for each anion investigated and each separation mode were calculated in accordance with DIN 32645 [40] and are summarized in Table 3. The PMA electrolyte buffered by TEA only showed a slight better performance because of its higher ionic strength causing in a more pronounced electrophoretic preconcentration while applying the separation voltage [41].

4. Conclusion

The composition of the widely used PMA electrolyte was thoroughly investigated because of the troubles in adjusting the pH of the laboratory-made electrolyte. During the ion exchange of the bromide salt some hexamethonioum is lost causing a lower HMOH concentration compared to the nominal weighted in concentration. Using this HMOH solution the pH of the electrolyte consisting of 2.25 mmol l^{-1} PMA, 6.5 mmol l^{-1} NaOH, 0.75 mmol l^{-1} HMOH and 1.6 mmol l^{-1} TEA was in the specified range of pH 7.8±0.1 [2]. The commercially available electrolyte fulfilled the pH specification but differed in the composition of NaOH, hexamethonium and TEA from the specification of Ref. [2].

Table 3
Detection limits for commercial available PMA electrolyte and self-prepared PMA electrolyte buffered by TEA only regarding the investigated injection mode in accordance with DIN 32645 [40]

	Concentration (μmol l^{-1})					
	Hydrodynamic injection		Sample stacking		Electrokinetic injection with transient isotachophoretic preconcentration	
	Commercial electrolyte	TEA buffered electrolyte	Commercial electrolyte	TEA buffered electrolyte	Commercial electrolyte	TEA buffered electrolyte
Bromide	1.7	1.4	0.22	0.20	0.015	0.014
Chloride	2.9	2.2	0.32	0.22	0.018	0.013
Sulfate	1.4	0.6	0.33	0.23	0.021	0.016
Nitrite	0.9	0.4	0.38	0.35	0.019	0.010
Nitrate	1.7	1.9	0.40	0.12	0.015	0.013
Oxalate	1.9	1.9	0.29	0.12	0.020	0.017
Fluoride	2.0	2.7	0.42	0.29	0.012	0.010
Formate	1.2	1.7	0.22	0.19	0.014	0.009
Phosphate	1.9	1.5	0.20	0.06	0.015	0.012

An electrolyte buffered by TEA only was proposed to improve the robustness of the laboratory preparation and statistical validated by Taguchi's methodology combined with ANOVA. No statistically significant difference could be detected between the commercial electrolyte and a self-prepared electrolyte buffered by TEA only considering the calibrations of hydrodynamic, stacking and electrokinetic injection with transient isotachophoretic preconcentration as well as migration times repeatability, peak symmetries and resolutions. Thus, an electrolyte consisting of 2.25 mmol l^{-1} PMA, 0.75 mmol l^{-1} HMOH and 12 mmol l^{-1} TEA was proved to be equivalent regarding the performance and as superior to the commercial one because of both the simplified pH adjustment and inherent greater buffer capacity.

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