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Simultaneous determination of inorganic anions and cations in waters by capillary electrophoresis

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Abstract

The applicability of a recently proposed capillary electrophoresis technique based on the electromigrative sample introduction from both ends of the capillary was further investigated for the simultaneous determination of inorganic anions and cations in real water samples. The optimized separations were carried out in 5.0 mmol l⁻¹ copper(II)–ethylenediaminehydroxide and 2.0 mmol l⁻¹ triethanolamine electrolyte neutralized with chromic acid to pH 8.0, using indirect UV detection at 254 nm. Nine inorganic ions (Cl⁻, NO₃⁻, SO₄²⁻, HCO₃⁻, K⁺, NH₄⁺, Na⁺, Ca²⁺ and Mg²⁺) were well separated in less than 5 min. The analytical performance of the method is discussed in terms of migration time, peak area and corrected peak area repeatability, linearity of response and detection limits. To evaluate this system, the determination of anions and cations was examined for mineral water, tap water and river water samples using Li⁺ as the internal standard. The comparison of the results with ion chromatography and conventional capillary electrophoresis is presented. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Common inorganic anions and cations are monitored routinely in a wide variety of water samples such as mineral waters, tap waters, groundwaters, etc. Therefore, a simple and convenient method that can simultaneously determine all major cations and anions in natural water samples would be very useful for routine analysis.

The most common analysis method used for such samples in the last decade is ion chromatography (IC) [1]. However, the determination of anions and

cations using IC technique requires entirely different conditions (stationary and mobile phases). The use of two separate analysis, one for the anions and other for the cations, is labor intensive as well as time consuming.

In recent years the use of capillary electrophoresis (CE) for the analysis of ionic analytes has grown significantly. Because of its higher resolution, shorter analysis time, lower consumption of reagents, and greater simplicity in operation compared to IC [2], CE has received a great deal of attention for the determination of inorganic ions. Numerous applications of CE have been reported for the determination of alkaline and alkaline earth cations [3–9] and common inorganic anions [10–18] in various aque-

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ous samples. However, as the separation by CE is based on the difference in electrophoretic mobilities of the analytes, the determination of fast anions and cations in a single analysis under conventional CE conditions is not possible.

In our previous work [19] we have proposed a new approach for a simultaneous CE separation of inorganic anions and cations based on electromigration sample introduction from both ends of the capillary and indirect UV detection. This approach requires the capillary with the detector window placed approximately in the middle of the capillary. An electrolyte system based on copper(II)–ethylenediaminenitrate was developed for the simultaneous indirect UV detection of NH_4^+ , K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} and HCO_3^- ions. Simultaneously Kuban and Karlberg [20] described a similar approach for the simultaneous CE separation of small anions and cations based on two separate manual hydrodynamic injections of the sample into both ends of the capillary with a duration of 40 s. However, both these papers were focused only on the optimization of the separation conditions, e.g., choice of the electrolyte composition, pH, etc.

The main aim of this work was to investigate the applicability of our previously reported approach for the quantitative analysis. The method was applied to samples of mineral, tap and river water for the analysis of chloride, nitrate sulphate, hydrogencarbonate, sodium, calcium and magnesium ions using lithium as an internal standard for both anionic and cationic analytes. The results obtained are compared with the data of the same samples analyzed by IC and conventional CE.

2. Experimental

2.1. Instrumentation

Separations were performed on a P/ACE 2100 apparatus (Beckman Instruments, Fullerton, CA, USA) equipped with a UV detector with wavelength filters (200, 214, 230 and 254 nm). Fused-silica capillaries (Polymicro Technology, Phoenix, AZ, USA) of 75 μm I.D. \times 375 μm O.D. and 72 cm total length (50 cm to the detector) were used. Samples were introduced by electromigration injection (5 kV;

5 s). Two vials were filled with a sample solution. Then both capillary ends were soaked in the sample vials and electromigrative injection was performed. System Gold software was used for data acquisition. Indirect UV detection was employed at 254 nm. All experiments were conducted at 25°C.

A Dionex 2000i/SP IC system (Dionex, Sunnyvale, CA, USA) equipped with a conductivity detector and micro-membrane suppressors was used for IC determination. The IC separations were carried out on an IonPac CS2 (for cations) and AS3 (for anions) columns (250 \times 4 mm I.D.).

2.2. Reagents and solutions

All solutions, electrolytes and standards were prepared with ultra-pure water from a Milli-Q system (Millipore, Eschborn, Germany). Ethylenediamine (En) and triethanolamine (TrEA) were purchased from Sigma (St. Louis, MO, USA). All other reagents were of analytical-reagent grade obtained from Merck (Darmstadt, Germany).

Stock solutions (0.01 mol l^{-1}) of analyte ions were prepared from inorganic salts. Stock solutions and samples were diluted to the desired concentration with 1 mmol l^{-1} TrEA borate solution (pH 8.0) before introduction. A 0.1 mol l^{-1} En and a 0.1 mol l^{-1} TrEA solution were used for the preparation of the carrier electrolytes.

Chromic acid solution (0.1 mol l^{-1}) was prepared by dissolving of CrO_3 in water. Copper(II)–ethylenediaminehydroxide solution was prepared by dissolving $\text{Cu}(\text{OH})_2$ in the appropriate amount of En.

Tetradecyltrimethylammonium hydroxide (TTAOH) was prepared from tetradecyltrimethylammonium bromide by conversion using an OH^- form anion-exchange column.

2.3. Procedures

Each day before starting the analysis, the capillary was rinsed with 0.1 mol l^{-1} NaOH and water for 5 min, followed by the used carrier electrolyte for 25 min. Between all electrophoretic separations the capillary was rinsed for 2 min with carrier electrolyte. All electrolyte solutions were filtered through a 0.45- μm membrane filter and degassed by ultrasonication.

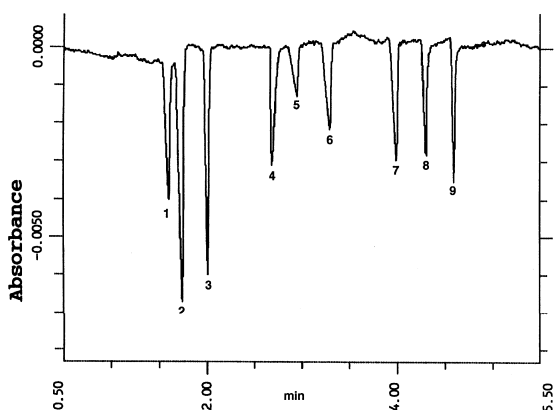


Fig. 1. Electropherogram of a mixed cation-anion standard solution under optimum conditions. Electrolyte, 5 mmol l⁻¹ Cu(En)₂²⁺-hydroxide, 2 mmol l⁻¹ TrEA and 20 μmol l⁻¹ TTAOH; pH 8.0 with chromic acid; capillary, 50 cm from anodic and 22 cm from cathodic end to detector; applied voltage, 25 kV; electromigration (5 s, 5 kV) injection from both ends of the capillary; indirect UV detection at 254 nm. Analyte concentrations: 5 × 10⁻⁵ mol l⁻¹ K⁺, Ca²⁺ and Mg²⁺, 1 × 10⁻⁴ mol l⁻¹ Na⁺, NH₄⁺, Cl⁻, HCO₃⁻ and SO₄²⁻, 2.5 × 10⁻⁴ mol l⁻¹ NO₃⁻. Peaks: (1) Cl⁻; (2) NO₃⁻; (3) SO₄²⁻; (4) HCO₃⁻; (5) K⁺; (6) NH₄⁺; (7) Na⁺; (8) Ca²⁺; (9) Mg²⁺.

IC analysis of water samples was performed according to the procedures described in Refs. [21–23] and conventional CE analysis as described in Refs. [24,25].

3. Results and discussion

3.1. Electrolyte composition

In our previous work [19] for the simultaneous CE separation of common inorganic anions and cations based on the electromigrative sample introduction from both ends of the capillary and indirect UV detection at 214 nm, we introduced a new electrolyte system containing two UV chromophores: cationic copper(II) chelate with ethylenediamine [Cu(En)₂²⁺] and an anion of nitrate. However, more detailed experiments showed that using this electrolyte, relatively high pH changes of more than 0.2–0.5 pH units resulting from electrolysis by the separation voltage were observed after 10–12 runs. These pH fluctuations in the carrier electrolyte influence electroosmotic flow (EOF) and, therefore, the migration

times of all analytes. In addition, detection properties of analytes change with pH due to the poorer baseline stability, leading to higher limits of detection. Moreover, the use of nitrate ion as anionic UV-chromophore eliminates the possibility to determine NO₃⁻ ions in the same run. In this study we have substituted nitrate by chromate, which is widely used in the CE of fast inorganic anions [10–12]. Sodium, potassium or ammonium chromate should not be used because these cations are potential analyte ions. Therefore chromic acid (H₂CrO₄) was added to the Cu(En)₂²⁺-hydroxide solution. A comparison of the separations achieved with electrolyte containing 5 mmol l⁻¹ Cu(En)₂²⁺-hydroxide neutralized with nitric and chromic acids to pH 8.0 showed that chromate provided the better overall performance for the simultaneous separation of cations and anions investigated in this study, despite a small loss in detection sensitivity of cations resulting from the fact that molar absorptivity for Cu(En)₂²⁺ chelate at 254 nm is less than at 214 nm. For example, the separation of Na⁺, Ca²⁺ and Mg²⁺ cations with chromate-based carrier electrolyte is excellent and any addition of weak complexing agent, such as fumaric acid, in this case is not necessary. The explanation of this fact can be attributed to the partial formation of the neutral species MCrO₄ (for Ca²⁺ and Mg²⁺), resulting in a reduction of the mobility of the both cations with respect to sodium ions. However, when using a chromate-based electrolyte potassium and hydrogencarbonate ions comigrate. This problem can easily be solved in two ways: (1) by changing the ratio of the capillary lengths before and after detector window or (2) by reduction of the EOF. The second approach was adopted in this study. An addition of 20 μmol l⁻¹ of TTAOH to the electrolyte slightly reduces the migration times for anions and increases those for all cations, so K⁺ and HCO₃⁻ are fully separated. Finally, for the suppression of pH fluctuations during the separations a 2 mmol l⁻¹ triethanolamine was additionally added to the carrier electrolyte. This base (pK_a = 7.9) was successfully used for buffering of the electrolyte by CE separations of inorganic anions [8]. Its cation, having a low mobility, does not cause a system peak and, consequently, does not interfere in the determination of analytes studied. Moreover, triethanolamine forms complexes with

most transition metal cations and prevents their precipitation at higher pH.

A carrier electrolyte with the following composition was chosen for all further studies: 5 mmol l⁻¹ Cu(En)₂²⁺-hydroxide, 2 mmol l⁻¹ TrEA and 20 μmol l⁻¹ TTAOH neutralized with chromic acid to pH 8.0. Fig. 1 shows an electropherogram of a mixed cation–anion standard solution under optimum conditions. As can be seen, this modified electrolyte enables the separation of all anions and cations studied in less than 5 min. This electrolyte solution was stable at least for 6 months.

It is interesting to note that copper(II) chelate with ethylenediamine significantly improves the resolution between Cl⁻ and SO₄²⁻ anions due to the reduction of the migration time of SO₄²⁻. This phenomenon is illustrated by the electropherograms in Fig. 2, where the separation of these two anions under the same

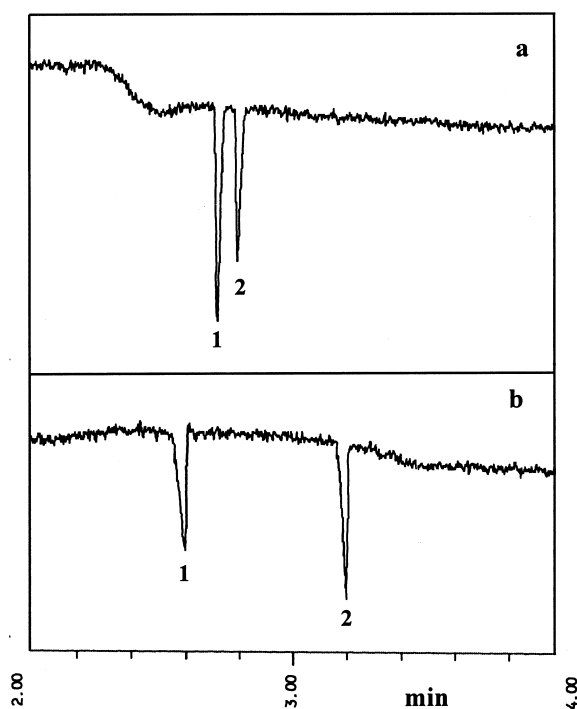


Fig. 2. Separation of Cl⁻ and SO₄²⁻ anions using (a) Na₂CrO₄ and (b) [Cu(En)₂][CrO₄] electrolytes. Electrolyte, 5 mmol l⁻¹ chromate, 0.2 mmol l⁻¹ TTAOH; pH 8.0; applied voltage, -25 kV; electromigration (5 s, 5 kV) injection from cathodic end; other conditions as in Fig. 1. Peaks: (1) Cl⁻; (2) SO₄²⁻.

conditions (except electrolyte counter-ion) is compared. The current values achieved in both cases were similar [18.7 and 19.5 μA for Cu(En)₂²⁺ and Na⁺ counter-ions, respectively] so the improvement in the resolution of -1 and -2 charged analytes resulting from the differences in the electrolyte ionic strength was negligible [26]. A possible explanation of this effect involves ion pairing between Cu(En)₂²⁺ and sulphate.

3.2. Validation of the method

The use of electromigrative sample introduction mode causes two biases concerning quantitative analysis [27]. One is brought about by the different mobilities of the species in the sample solution. This effect causes a distortion in the ratio of peak areas for ions having different mobilities.

The other effect is related to the ionic strength of the medium in which the analytes are dissolved. If the ionic strength of the sample varies significantly from that of the standard solution systematic errors are possible, because the amount of analyte injected depends on the total ionic strength of the sample. Both these biases can be minimized or entirely eliminated by using an internal standard for the quantitative analysis. This approach is also time saving because it requires only one run per sample. It should be noted, that the quantitative analysis of very low ionic strength samples such as high purity water is also possible using standard addition or conventional calibration graph techniques [13,28].

In this study we have investigated Li⁺ (as its tetraborate salt) cation as the internal standard for both anionic and cationic analytes. This choice is based on the fact that the lithium concentration is below the limit of detection in most water samples. A 1 × 10⁻⁴ mol l⁻¹ concentration of Li⁺ was used in all determinations.

The pH of the sample solution can effect the determination of ions using an electromigrative sample introduction technique. The pH of the sample controls the mobility of analytes of weak acids during the injection procedure. The analytes display changes in electrophoretic mobility if the pH is changed in the vicinity of their pK_a. While most ions

Table 1

Migration time and peak area repeatability (1×10^{-4} mol l⁻¹ of each analyte; six replicate injections)

Analyte	Migration time R.S.D. (%)	Peak area R.S.D. (%)	Time-corrected peak area R.S.D. (%)
Cl ⁻	0.26	2.4	2.1
NO ₃ ⁻	0.21	2.2	2.3
SO ₄ ²⁻	0.18	2.1	1.9
HCO ₃ ⁻	0.45	5.2	5.3
K ⁺	0.31	2.6	2.4
NH ₄ ⁺	0.36	5.0	4.5
Na ⁺	0.24	2.4	2.0
Ca ²⁺	0.25	2.2	1.8
Mg ²⁺	0.20	1.8	1.6

Separation conditions as in Fig. 1.

studied are unaffected by pH changes, some analytes such as hydrogencarbonate and ammonium can display changes in apparent mobility due to small changes in pH. Consequently all standards and samples were dissolved in a 1 mmol l⁻¹ TrEAborate solution (pH 8.0). An injection of this pure solution did not show any presence of impurities, especially the analytes of interest.

Repeatability experiments of migration times, peak areas and time-corrected peak areas were performed for 1×10^{-4} mol l⁻¹ standard solutions (Table 1). As can be seen the repeatability in terms of peak area was between 1.8 and 5.2% relative standard deviation (R.S.D.), depending on the analyte. Ammonium and hydrogencarbonate determinations showed the worst repeatability with 5.0 and 5.2% R.S.D., respectively. The higher R.S.D. values for ammonium probably can be explained by the

little fluctuations of the pH of the carrier electrolyte which causes changes in the effective charges for this weakly acidic analyte ($pK_a=9.25$) and for hydrogencarbonate by absorption of carbon dioxide from the atmosphere. Similar R.S.D. values were achieved also for corrected peak areas. The repeatability in terms of migration times was less than 0.5% R.S.D. for all analytes studied.

The linearity of the calibration curve was evaluated in the range 1×10^{-5} – 1×10^{-3} mol l⁻¹ for each analyte using 1×10^{-4} mol l⁻¹ Li⁺ as internal standard. For the evaluation of calibration curves the peak areas of the analytes were divided by the peak area of the internal standard. Valid calibration is demonstrated over 1.5 order of magnitude. The calibration data for all analytes are presented in Table 2. The y intercept value was the highest for hydrogencarbonate because in water samples ex-

Table 2

Calibration data and detection limits for ions studied

Analyte	Linear range (mol l ⁻¹)	Equation of regression lines	Correlation coefficient (r ²)	Detection limit (mg l ⁻¹)
Cl ⁻	2×10^{-5} – 1×10^{-3}	$y = -0.0184 + 0.686 \times 10^4 c$	0.998	0.3
NO ₃ ⁻	2×10^{-5} – 1×10^{-3}	$y = -0.0422 + 0.704 \times 10^4 c$	0.999	0.5
SO ₄ ²⁻	1×10^{-5} – 5×10^{-4}	$y = -0.0037 + 1.402 \times 10^4 c$	0.999	0.5
HCO ₃ ⁻	2×10^{-5} – 1×10^{-3}	$y = 0.0814 + 0.664 \times 10^4 c$	0.996	0.8
K ⁺	2×10^{-5} – 1×10^{-3}	$y = 0.0293 + 0.815 \times 10^4 c$	0.998	0.6
NH ₄ ⁺	2×10^{-5} – 1×10^{-3}	$y = -0.0148 + 0.647 \times 10^4 c$	0.997	0.2
Na ⁺	2×10^{-5} – 1×10^{-3}	$y = 0.0255 + 0.827 \times 10^4 c$	0.998	0.3
Ca ²⁺	1×10^{-5} – 5×10^{-4}	$y = 0.0195 + 1.41 \times 10^4 c$	0.999	0.2
Mg ²⁺	1×10^{-5} – 5×10^{-4}	$y = 0.0231 + 1.47 \times 10^4 c$	0.999	0.1

posed to the atmosphere it equilibrates by absorption of carbon dioxide in water, reaching concentrations of $\sim 10^{-5} \text{ mol l}^{-1}$ within several minutes.

The limits of detection achieved with $\text{Cu}(\text{En})_2^{2+}$ – chromate electrolyte system also are given in Table 2. These detection limits were determined for electromigrative injection at 5 kV for 5 s based on three times the baseline noise. The detection limits can be reduced by increasing of the amounts injected either by increasing the injection time or increasing the injection voltage. Further, the detection sensitivity can be significantly improved by injection of low ionic strength solutions (stacking conditions) without loss of efficiency [13]. For instance, all analytes at a $10^{-6} \text{ mol l}^{-1}$ concentration are not detected if diluted with a 1 mmol l^{-1} TrEA–borate solution, but they are detected without difficulty at this concentration if the same sample is diluted in deionized water. Such approach for the simultaneous determination of anions and cations in high purity waters will be the aim of our further investigations.

The slope values for singly charged anions (chloride, nitrate and hydrogencarbonate) are about half of those for the doubly charged sulphate. The slopes of the calibration plots for doubly charged Ca^{2+} and Mg^{2+} cations are only about 1.75 times higher, e.g., lower than predicted theoretically, than those for Na^+ and K^+ due to the partial complexation of these analytes with chromate and/or with hydroxide ions. Finally, with the pH of the carrier electrolyte at 8.0, the protonation of ammonium is not complete and the lower value of the slope reflects an effective charge smaller than +1 for that cation.

3.3. Water analysis

To evaluate this system for real samples, it was applied to the determination of common inorganic anions and cations in a mineral, tap and river water samples. Fig. 3 shows the typical electropherograms for the river water (a) and tap water (b) sample solutions. The determination does not require any preliminary treatment of the samples except addition of an internal standard and dilution. Only mineral water samples with high content of dissolved carbon dioxide were degassed by sonication. The results are summarized and compared with two alternative techniques in Table 3. As can be seen, the method

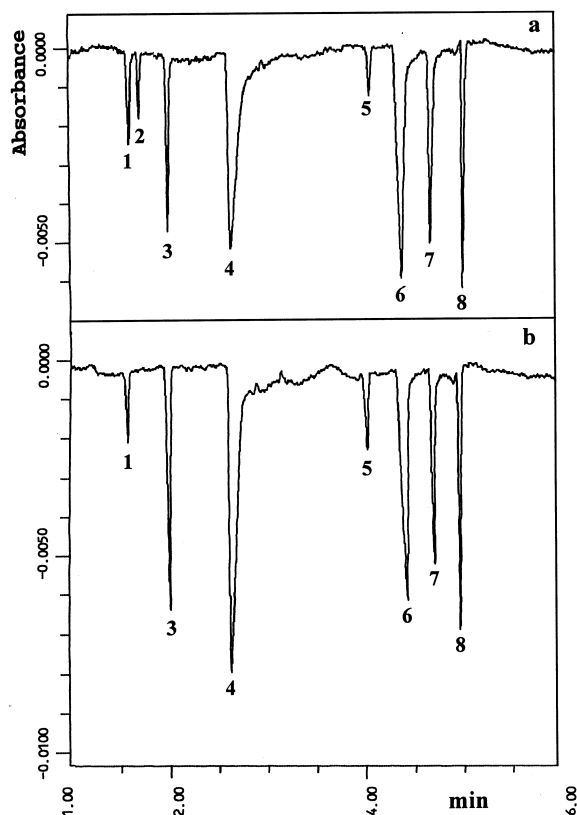


Fig. 3. CE analysis of (a) river water and (b) tap water samples (dilution 1:5). Conditions as in Fig. 1. Peaks: (1) Cl^- ; (2) NO_3^- ; (3) SO_4^{2-} ; (4) HCO_3^- ; (5) Na^+ ; (6) Ca^{2+} ; (7) Mg^{2+} ; (8) Li^+ (internal standard).

showed good agreement with data obtained from ion chromatography [21–23] and conventional capillary electrophoresis [24,25].

In conclusion, the above results show that capillary electrophoresis offers a unique possibility for determination of common inorganic anions and cations in a single run. The proposed system is simple, rapid and is sufficiently sensitive and precise to be useful for the analysis of natural water samples.

Acknowledgements

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Table 3
Data comparison (mg l⁻¹) of water samples (n=5)

Sample	Analyte	CE ^a	IC	Conventional CE
Tap water (1:5)	Cl ⁻	21.4 (2.4)	23.1	23.0
	SO ₄ ²⁻	39.0 (1.9)	37.4	40.5
	HCO ₃ ⁻	186 (3.4)	165 ^b	170
	Ca ²⁺	66.3 (2.9)	63.4	66.9
	Na ⁺	17.9 (2.8)	16.8	16.5
	Mg ²⁺	19.8 (2.6)	20.6	21.0
Neris river water (1:5)	Cl ⁻	28.6 (2.2)	26.4	26.6
	NO ₃ ⁻	21.2 (2.3)	19.1	23.5
	SO ₄ ²⁻	26.5 (2.1)	27.9	28.0
	HCO ₃ ⁻	132 (4.1)	154 ^a	139
	Ca ²⁺	74.0 (2.5)	70.7	72.0
	Na ⁺	14.5 (3.1)	14.2	15.4
Mineral water 'Vytautas' (1:200)	Mg ²⁺	22.6 (2.6)	24.1	22.9
	Cl ⁻	3450 (2.4)	3580	3520
	SO ₄ ²⁻	980 (2.8)	1020	1080
	HCO ₃ ⁻	253 (6.3)	278 ^b	280
	Ca ²⁺	592 (2.7)	575	579
	Na ⁺	1830 (2.0)	1740	1810
	Mg ²⁺	254 (3.1)	260	268

^aValues in parentheses are relative standard deviations (%).

^bTitrimetric determination.

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