

Technical paper

Accurately Determining Hydrogen Carbonate in Water in the Presence of or Simultaneously with the Anions of Carboxylic Acids

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Abstract

The first objective of our investigation was to find an experimental procedure and conditions under which ion-exclusion chromatography gives reliable results for determining the concentration of hydrogen carbonate in model solutions: results that are comparable with other traditional methods, e.g., potentiometric titration and direct potentiometry with a CO₂-responsive electrode. Our second aim was to estimate the effect of anions of carboxylic acid on the hydrogen carbonate determination with different analytical methods. The extent of the possible interferences was evaluated afterwards with ion-exclusion chromatography for real samples, i.e., surface waters. The analyses of the Slovenian river waters and waste water from a paper-production plant are represented as a pilot study for the method comparison for real life applications. Ion-exclusion chromatography was recognised as the method of choice for a reliable determination of the concentration of hydrogen carbonate in water samples containing anions of carboxylic acids.

Keywords: hydrogen carbonate/bicarbonate, ion-exclusion chromatography, potentiometric titration, direct potentiometry, river water, waste water

1. Introduction

The simple and accurate determination of carbonate species is an important requirement in water purification, diagenetic modelling, oilfield inorganic-scale-precipitation estimations, predicting the extent of acidification of lakes and rivers as well as environmental and biological research. One of the very basic analytical parameters frequently determined in natural waters and effluents, and arising out of knowledge of the chemistry of the carbonate species in waters is alkalinity. There are several areas which use alkalinity and derive calculations, interpretations and conclusions from it. Such examples are a simplified approach to assessment of excess carbon dioxide partial pressure in natural waters,¹ theoretical calculation model for estimating the acidification capacity of natural waters,² estimating organic acid dissociation in natural surface waters,³ designing of a waste water treatment,⁴ and assessments of calcite saturation.^{5–7}

Alkalinity which is determined by a titration is a measure of the ability of water body to neutralise acidity. A definition of alkalinity takes into account the important proton-accepting components of natural waters which are primarily hydrogen carbonate – bicarbonate ions (HCO₃⁻), carbonate ions (CO₃²⁻) and hydroxyl ions (OH⁻). Hydrogen carbonate is a strongly prevailing component in natural unpolluted waters with moderately basic pH; and contribu-

tions of carbonate and hydroxyl ions to the total alkalinity can be considered negligible. In such cases the alkalinity can be denoted to hydrogen carbonate only and understood as the hydrogen carbonate concentration determination, contributing to the simplification of further interpretations. But this is true only as far as no other proton-accepting components are present in natural water or their concentrations can be considered negligible too. Anions of carboxylic acids are among possible interferences affecting the hydrogen carbonate determination and as recognised by different authors the systematic error in titrimetric determination influences the reliability of the model predictions.^{1–3}

This study aims at assessing the accuracy of the hydrogen carbonate determination in water samples by different analytical methods in the presence of the anions of carboxylic acids. Evaluation comprises potentiometric titration, direct potentiometry and ion-exclusion chromatography. During past decades, ion-exclusion chromatography has been developed to become one of the leading analytical techniques for the separation and determination of short-chain aliphatic carboxylic acids in various matrices, e.g., soil, air, ground water, drinking water, geological materials, sewage, waste and biomass.⁸ Although a carbonate peak is often observed using ion-exclusion chromatography, this peak has only seldom been used to determine the concentration of carbonate species.^{9–11} The two main reasons for this were recognised by Tanaka and Ishizuka;⁹

the low sensitivity and the narrow linear range of the calibration curve. Atmospheric carbon dioxide dissolved in the eluent was considered as the cause of this problem. As we demonstrate in this work carbon dioxide present in the sample represents a serious difficulty too since it increases the final result. Therefore, for a reliable determination of the concentration of hydrogen carbonate, the removal of carbon dioxide from the sample prior to the sample injection is required, and the procedure needs to be simple and fast.

The first objective of our investigation was to find an experimental procedure and conditions under which ion-exclusion chromatography gives reliable results for determining the concentration of hydrogen carbonate in model solutions: results that are comparable with other traditional methods, e.g., potentiometric titration and direct potentiometry with a CO₂-responsive electrode. Our second aim was to estimate the effect of anions of carboxylic acid on the hydrogen carbonate determination with different analytical methods. The extent of the possible interferences was evaluated afterwards with ion-exclusion chromatography for real samples, i.e., surface waters. The analyses of the Slovenian river waters and waste water from a paper-production plant are represented as a pilot study for the method comparison for real life applications.

2. Experimental

2.1. Instrumentation

A Dionex 4000i (Dionex Corporation, USA) ion chromatograph was used. This consisted of the following components: an eluent degas module, a gradient pump module, an injector with a 50- μ L injection loop, a IonPac ICE-AS1 (9 \times 250 mm) chromatographic column, a AMMS-ICE (4 mm) micromembrane suppressor and a conductivity detector. The output of the detector was connected to a ChromJet integrator (Thermo Separation Products, USA).

Potentiometric titrations were performed with a 716 DMS Titrino (Metrohm, Switzerland) automatic titrator. This was equipped with a 5-mL exchange unit, a 728 stirrer, a combined pH glass electrode (6.0204.100) and a Pt 1000 temperature sensor. The visualisation of the titration curves was made possible by WinWedge – RS232 data-acquisition software (TAL Technologies, USA), which inputs serial data, obtained from the titrator, directly into the Excel program.

An Orion, Model 95–02 carbon dioxide responsive electrode (Orion Research, Inc., USA) and a MA5740 pH-meter (Iskra, Slovenia) were used for the direct potentiometry.

2.2. Chemicals

Standard solutions of hydrogen carbonate, acetate, formiate and lactate were prepared from NaHCO₃,

CH₃COONa, HCOONa, C₆H₁₀CaO₆ · 5H₂O. All the chemicals were analytical grade reagents. A stock eluent solution of heptafluorobutyric acid (10 mmol L⁻¹) was prepared from a chemical (>99%) purchased from Fluka (Switzerland). A heptafluorobutyric acid eluent (1 mmol L⁻¹) was obtained from the stock solution by a 10-fold dilution. Tetrabutylammonium hydroxide (>99%, Fluka, Switzerland) was used for the preparation of the regenerant solution with a concentration of 5 mmol L⁻¹. A standard solution of hydrochloric acid (0.1 mol L⁻¹) for the potentiometric titration was prepared from Titrisol 1.09973. (Merck, Germany). The carbon dioxide buffer (950210) and carbon dioxide standards (950206, 950207), which were used with the carbon dioxide electrode, were purchased from Orion Research, Inc. (USA). All the solutions were prepared with deionised water, additionally purified through a Milli-Q System (Millipore Corporation, USA) and degassed before use.

2.3. Prevention of Carbon Dioxide Interference During Chromatography

In order to remove the need for a one-hour-long bubbling of the eluent with nitrogen gas, a procedure that was suggested by Hayakawa et al.¹¹ to obtain reproducible peak heights, an alternative approach was used. The eluent solution was prepared with carbon-dioxide-free water. Analyses proved the effective carbon dioxide removal from deionised water in 15 min if a reduced pressure and sonification were applied simultaneously. After preparation, the eluent and regenerant solutions were kept under a nitrogen atmosphere in the ion chromatographs reservoirs. In order to prevent carbon dioxide interference in the real samples, carbon dioxide was removed from the samples prior to their injection into the chromatograph. A 3-way luer stopcock was positioned between a syringe and a filter holder. With the stopcock in the closed position the piston was pulled backwards causing a pressure reduction in the syringe, this resulted in the liberation of gases from the solution. The stopcock was then turned to the position that caused the gases to be pushed out of the syringe. The same procedure was repeated a few times. The stopcock was finally put into the position for injection. The sample passed the filter and filled the injection loop. This simple and fast at-line procedure for carbon dioxide removal from the water samples proved successful and appropriate for a reliable determination of the concentration of hydrogen carbonate.

3. Results and dDiscussion

3.1. Determination of Hydrogen Carbonate in Model Solutions

The three methods were first compared for the analysis of a model solution that contained hydrogen car-

bonate in a concentration of 3 mmol L⁻¹. As demonstrated in Table 1, there is good agreement between the final results obtained with the three methods; the titrimetric and chromatographic determinations matched especially well. The highest repeatability expressed as a relative standard deviation (RSD) was observed in potentiometric titration (0.13%), in contrast with the repeatabilities of ion-exclusion chromatography (1.9%) and direct potentiometry (3.5%) which were more comparable with the first being slightly better.

Table 1. Hydrogen carbonate determination in a model solution – a comparison of the results obtained with three different analytical methods mmol L⁻¹.

	Ion-exclusion chromatography		Titration	CO ₂ electrode
	<i>t_{Ri}</i> (min)	<i>c</i> (mmol L ⁻¹)	<i>c</i> (mmol L ⁻¹)	<i>c</i> (mmol L ⁻¹)
Average, <i>n</i> = 3	15.29	2.99	3.00	2.95
RSD (%), <i>n</i> = 3	0.038	1.9	0.13	3.5

The determination of hydrogen carbonate with ion-exclusion chromatography was examined in more detail: good linearity was observed. The correlation coefficient for the hydrogen carbonate determination on the conductivity detector output range 10 μS was 0.9999; the concentration range extended from 0.6 mmol L⁻¹ to 3.6 mmol L⁻¹. For a successive detector output range – 30 μS the correlation coefficient was 0.9981 and the concentrations of the calibration solutions were between 1 mmol L⁻¹ and 6 mmol L⁻¹. The between-day repeatability of the hydrogen carbonate determinations was examined at the 3 mmol L⁻¹ concentration level. The relative standard deviation was 3.6% (*n* = 7).

3.2. Effect of Carboxylic Acid Anions on Determination of Hydrogen Carbonate

The effect of anions of carboxylic acids on the hydrogen carbonate determination with different analytical methods was estimated for our measuring systems.

The possible interfering effect of anions of carboxylic acids (4 mmol L⁻¹) on the titrimetric determination of hydrogen carbonate was evaluated first (Table 2). Even though the end-point pH was affected by the addition of potentially interfering anions in all cases, the final results for the hydrogen carbonate concentration determinations were in most cases close to what was theoretically expected.

Table 2. Estimation of the effect of anions of carboxylic acids on the titrimetric determination of the hydrogen carbonate concentration in model solutions.

Carboxylic anion addition	none	tartrate	formiate	salicylate	oxalate	acetate
<i>c</i> HCO ₃ ⁻ (mmol L ⁻¹)	3.95	3.95	3.96	3.96	4.06	7.76

A slight effect on the final result was observed for oxalate. Acetate, on the other hand, interferes significantly with the hydrogen carbonate determination and the citrate prevents the identification of the titration end point.

With the increase in acetate concentration titration's end points are shifted towards higher titration reagent consumptions and the curve maxima are less clearly expressed. Overestimations of the hydrogen carbonate concentration, which were observed at acetate concentrations of 0.4 mmol L⁻¹, 0.8 mmol L⁻¹, 1.6 mmol L⁻¹ and 4 mmol L⁻¹, were as follows: 8.8%, 18.5%, 36.7% and 96.4%.

Acetate and formiate were expected to be interfering species for the potentiometric determination of hydrogen carbonate with a carbon-dioxide-sensing electrode. The 2 mmol L⁻¹ concentration of formiate and acetate increased the result for hydrogen carbonate at the 4 mmol L⁻¹ concentration level for 11 and 16% respectively. It can be concluded that direct potentiometry is approximately three times less sensitive to acetate interference than potentiometric titration.

3.3. Estimation of Interference of Carboxylic Acid Anions in Real Samples

In order to estimate the extent of the possible interference effects of anions of carboxylic acids for real samples, i.e., surface waters, a pilot study comprising several Slovenian river water samples was performed. Concentrations of anions of carboxylic acids were determined with ion-exclusion chromatography. Figure 1 shows a chroma-

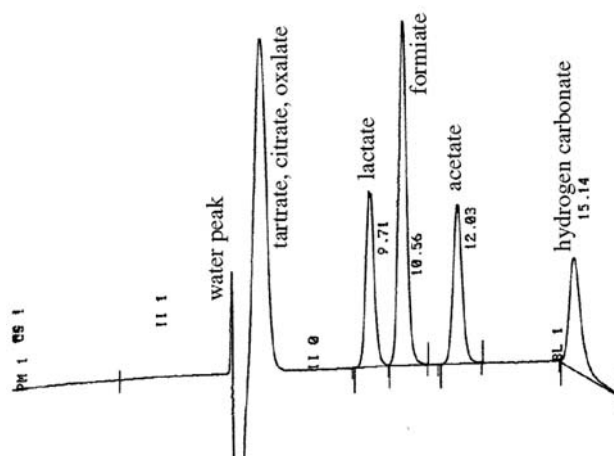


Figure 1. The chromatogram of the anions of carboxylic acids and hydrogen carbonate obtained with the IonPac ASE-1 column and conductivity detector.

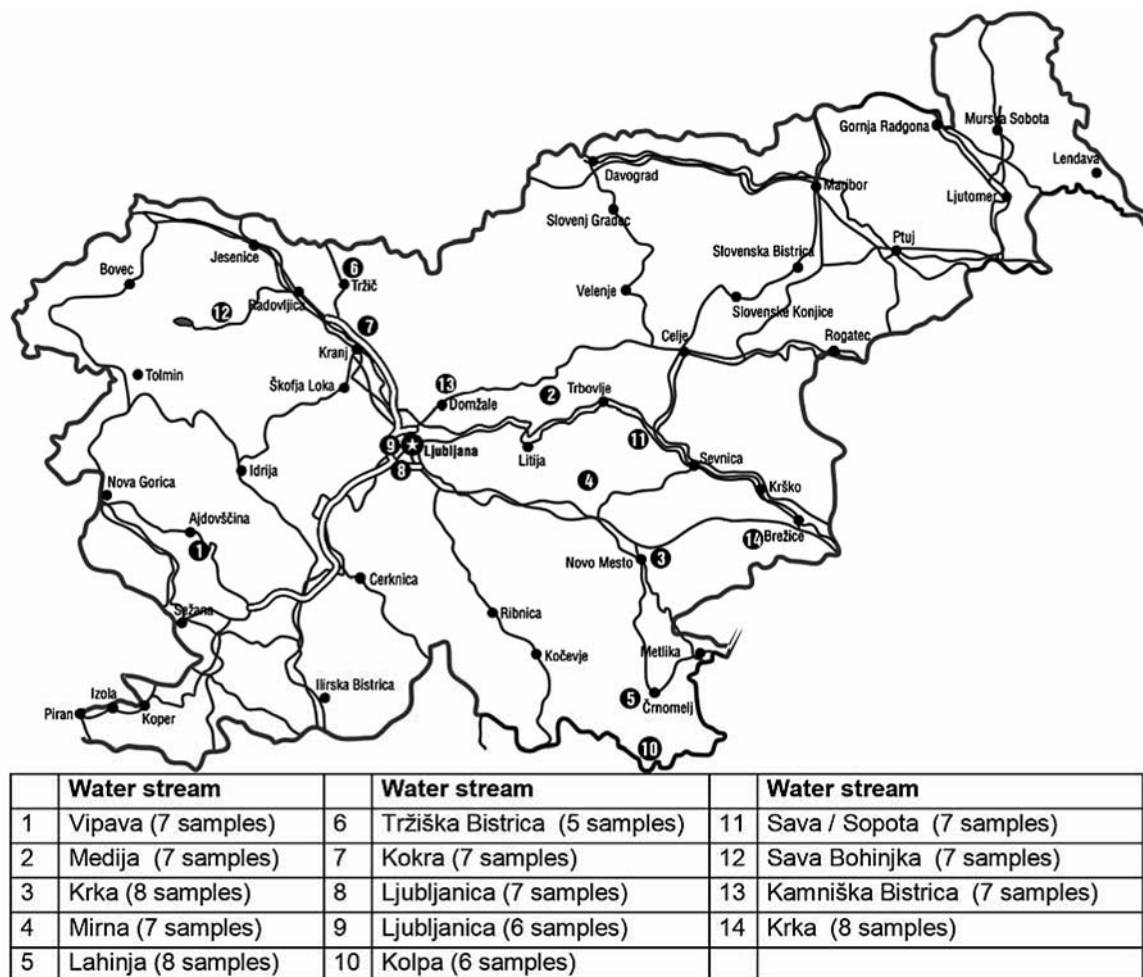


Figure 2. Approximate locations of rivers from which 97 water samples were taken at different locations.

togram obtained for a model solution with this analytical technique using a IonPac ASE-1 column and a conductivity detector.

In order to estimate the extent of the possible interference effects of anions of carboxylic acids for river water, samples were taken from different parts of Slovenia. Figure 2 shows the approximate locations of the rivers. Thirteen different water streams were sampled along the stream, 97 different samples were collected altogether. Detection of anions of carboxylic acids was only possible if a UV detector was used. An example of a typical chromatogram is presented in Figure 3. Hydrogen carbonate was determined simultaneously during the same run; however, in this case conductivity detection was used.

Lactate was detected in 32 samples and acetate in 22. Lactate concentrations were in the range between 5.6 and 72.8 $\mu\text{mol L}^{-1}$, with the statistical mean at 23.5 $\mu\text{mol L}^{-1}$ and the median at 21.0 $\mu\text{mol L}^{-1}$. The acetate concentrations ranged from 11.9 $\mu\text{mol L}^{-1}$ to 59.5 $\mu\text{mol L}^{-1}$. The mean concentration was at 31.5 $\mu\text{mol L}^{-1}$ and the median

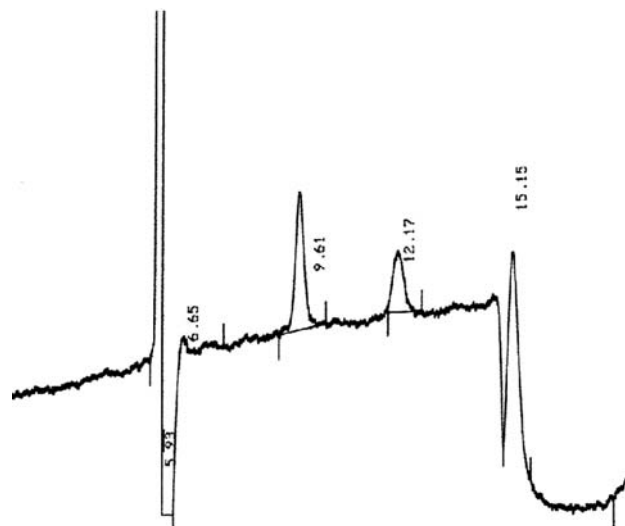


Figure 3. The chromatogram of the water sample from the Kolpa river obtained with UV detection. The chromatographic peak at 9.61 min corresponds to lactate; the peak with the retention time of 12.17 min is related to the acetate ion.

at $32.3 \mu\text{mol L}^{-1}$. No other anions of carboxylic acids were detected. The lowest hydrogen carbonate concentration observed in the examined samples was 0.97 mmol L^{-1} , and the highest was 5.74 mmol L^{-1} .

If we take into account the locations from which these 97 samples were taken, this group of samples might be considered a good representation of what can be expected for the Slovenian rivers in most cases. If we take into account concentrations of lactate, acetate and hydrogen carbonate found in real water samples with ion-exclusion chromatography and take into consideration, what we have previously learned about possible interferences for our measuring systems, an estimation of the impact of anions of carboxylic acids on hydrogen carbonate concentration determination in real samples can be made.

At the highest hydrogen carbonate concentrations found in Slovenian river waters the contribution of the acetate to the consumption of the titration reagent would usually be below 0.6%, and would not be expected to exceed a maximum of 1.0%. For moderate hydrogen carbonate concentrations the effect is expected to be no more than 1.5%, and in most cases it is lower. At very low hydrogen carbonate concentrations the contribution of the acetate to the result of the potentiometric titration is estimated to be between 1.2% and 6.1%, if there is some interfering effect.

3.4. Hydrogen Carbonate Determination in Surface Waters with Three Analytical Methods

In order to test the prediction from the previous section the results for hydrogen carbonate, which were obtained with ion-exclusion chromatography on the detector output range $10 \mu\text{S}$, were compared with the results of the potentiometric titration. The comparison included 21 samples. It was expected that slightly higher concentrations of hydrogen carbonate would be observed for the potentiometric titration. There were only four samples for which the results of the two methods were comparable, and one sample for which the concentration determined with ion-exclusion chromatography was nearly 10% lower. In all other cases the results obtained with ion chromatography were unexpectedly significantly higher than those obtained with potentiometric titration: twelve results were up to 15% higher, and four were more than 20% higher. The presence of carbon dioxide in the water samples was identified as a possible cause for the observed disagreement between the results obtained using the two methods.

Three river-water samples for which interferences of anions of carboxylic acids were expected were freshly sampled. A simple and fast at-line procedure for carbon dioxide removal from the water samples prior to injection into the chromatograph was introduced and tested as described in the experimental section. After the intro-

duction of this procedure the differences between the results obtained with the three different analytical methods were altered. The results are summarised in Table 3. Very good agreement was achieved for the results of ion-exclusion chromatography and direct potentiometry, especially for the samples from the rivers Ljubljanica and Gradaščica. For the river Trata, the result obtained with direct potentiometry was 3.4% higher than the ion-chromatographic determination. The potentiometric titration gave slightly higher results for the hydrogen carbonate determination, when compared with the results of the ion chromatography: from 2.8% to 6.2% higher. The expectation for the observed level of hydrogen carbonate, which was moderately high, was that the anions of the organic acids can increase the value of the results by approximately 1.5%.

Table 3. Hydrogen carbonate determination in river waters with three different analytical methods.

	Chromatography $c \text{ (mmol L}^{-1}\text{)}$	Titration $c \text{ (mmol L}^{-1}\text{)}$	CO_2 electrode $c \text{ (mmol L}^{-1}\text{)}$
Ljubljanica	3.66	3.78	3.67
Trata	3.56	3.66	3.68
Gradaščica	3.74	3.97	3.74

The titration curves for several real samples were thoroughly examined. It was observed that they were not as smooth in the equivalence-point region as they were when model solutions were titrated. It was also observed that the coefficient of variation for the hydrogen carbonate determinations in triplicates was much higher for the real samples – between 0.5% and 1.0% – than it was when the model solutions were titrated, i.e., 0.1%, in spite of the hydrogen carbonate concentration being higher in the real samples.

For the determination of hydrogen carbonate in the surface waters by potentiometric titration it can be concluded that if anions of the carboxylic acids are present, in spite of their low concentration level they can affect the hydrogen carbonate determination.

3.4. Analysis of Wastewater from Paper-Production Plants

All three analytical methods were used for the analysis of wastewater from a paper-production plant. A chromatogram obtained using a conductivity detector is presented in Figure 4. Anions of several organic acids were identified; their concentrations are higher and very different. The sample contained acetate in a concentration of 613 mg L^{-1} , lactate in a concentration of 415 mg L^{-1} , and formiate in a concentration of 16 mg L^{-1} . The hydrogen carbonate concentration was 122 mg L^{-1} .

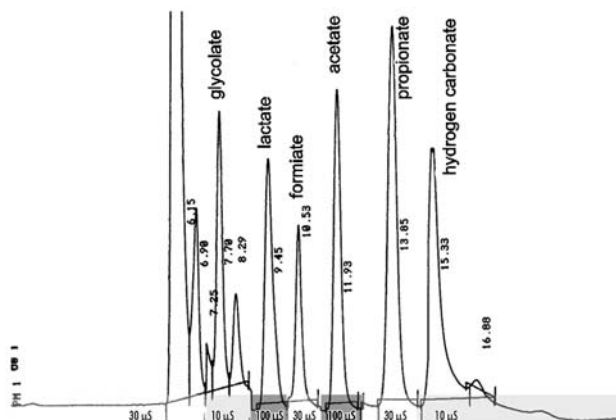


Figure 4. A chromatogram of wastewater from the paper-production plant. The conductivity detector output ranges were switched during the run between 30, 10 and 100 μS , as shown in the figure.

In the wastewater from the paper-production plant, hydrogen carbonate was impossible to determine using a potentiometric titration. If direct potentiometry was applied for the hydrogen carbonate determination in wastewater, the result obtained was 323 mg L^{-1} . This determination exceeds the ion-chromatographic determination by 165%, which is not at all surprising, since the acetate, which is only one of the potentially interfering anions identified in the wastewater sample with ion-exclusion chromatography, exceeds 10 mmol L^{-1} . A lack of awareness of the presence of interfering anions in the sample

would, in the case of direct potentiometry, lead to a completely erroneous result if the result was to have been assigned to the hydrogen carbonate concentration.

4. Acknowledgement

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5. References

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Povzetek

Prvi cilj raziskave je bil vzpostaviti eksperimentalni postopek in pogoje, pri katerih daje ionska izključitvena kromatografija zanesljive rezultate za določanje koncentracije hidrogenkarbonata v modelnih raztopinah, rezultate, ki so primerljivi z rezultati drugih tradicionalno uporabljenih analiznih metod kot sta potenciometrična titracija in neposredna potenciometrična določitev z elektrodo odzivno na CO_2 . Nadaljnji cilj je bil oceniti učinek anionov karboksilnih kislin na določanje hidrogenkarbonata z različnimi analiznimi tehnikami. Stopnjo pričakovanega vpliva interferenčnih ionov na določitev hidrogenkarbonata v realnih vzorcih npr. površinskih vodah smo ovrednotili z ionsko izključitveno kromatografijo. Na primeru analiz slovenskih rečnih vod in analize odpadne vode iz papirnice smo primerjali vse tri analizne metode. Ionska izključitvena kromatografija je metoda izbire za zanesljivo določanje koncentracije hidrogenkarbonata v vzorcih vod, ki vsebujejo anione karboksilnih kislin.