ION CHROMATOGRAPHY WITH CARBONATE ELUENTS. UV-DETECTOR RESPONSES TO SOME INORGANIC ANIONS

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Abstract. The UV-detector responses to four common anions (Cl^-, NO_3^-, HPO_4^{2-} and SO_4^{2-}) were measured by applying carbonate eluents in the suppressed and the non-suppressed mode. It was found that in the nonsuppressed mode the UV-detector responses to chloride, phosphate and sulfate ions were negative, but to nitrate ions they were in the normal direction, i.e. positive. In the suppressed mode, when the Na^+ cations were replaced by hydrogen ions, all the UV-detector responses were found to be positive.

Key words: ion chromatography, ultraviolet detector, detector responses to common anions.

The technique of ion chromatography has gained wide acceptance in the analysis of inorganic anions in a variety of aqueous matrices [1, 2]. It involves separation of the ions of interest on a low-capacity ion-exchange column typically followed by a conductivity detector. In order to attain low detection limits for the ions to be determined a suppressor device is often used between the separator column and the conductometric detector. On the other hand, if a UV-detector is applied there is no need for the suppressor device. But, according to a widely held belief, most inorganic ions lack suitable chromophores for UV-detection [3–5]. This is not always the case, especially when we are dealing with some common inorganic ions [3, 6–8]. The aim of this work was to examine the UV-detector response to some inorganic ions eluted from the separator column by carbonate eluents using both the single column and the suppressed technique. The latter converts dissolved Na_2CO_3 to $H_2CO_3 = H_2O + CO_2$. This conversion has remarkable effects on the UV-detector response to the inorganic anions studied, as shown below.

EXPERIMENTAL

A model IVK11 ion chromatograph (Design Office, Estonian Academy of Sciences) was used throughout the study. It was equipped with a UV-detector, i.e. a variable wavelength monitor from Knauer (Germany).

The chromatograms were recorded on a Servogor S recorder (Goerz, Germany). The separator column used (4×250 mm) was packed with HIKS-1 resin (Khimifil, Tallinn) with a capacity of 0.052 mequiv./cm³. The 4×250 mm suppressor column (if used) was packed with Dowex WX16 (20—50 mesh) cation exchange resin in H-form. A 0.43 ml sample loop was used for all injections. All solutions were made of analytical-grade chemicals by dissolving them in CO_2-free distilled water. The carbonate eluent used was prepared by dissolving 0.43 g of Na_2CO_3 in distilled water. The eluting efficiency of this eluent is approximately equal to that of the standard carbonate eluent (3.0 mM $NaHCO_3$/2.4 mM Na_2CO_3) [9].

The responses of the Knauer UV-monitor were compared to the absorbances measured on a spectrophotometer. For this purpose we used a Specord M40 (Carl Zeiss, Jena) with quartz cells (1 cm pathlength). The solutions used in the sample and reference cells are given in the respective figure captions.

RESULTS AND DISCUSSION

The UV-detector responses were recorded for the following ions: chloride, nitrate, sulfate and phosphate. For each of these ions the detector response was measured as a peak height, with the same test solution injected at different wavelengths (see Figs. 1—4). Two sets of experiments were carried out with each ion: (1) using a single-column system, i.e. with a nonsuppressed carbonate eluent (pH=10.9), and (2) using a dual-column system, i.e. with a suppressed eluent (pH=4.5). In the last case the eluent was converted into a water solution containing 4 mM H_2CO_3. The UV-detector responses to the ions studied may be divided into two groups: (1) the NO_3^- ions yielded a positive response in both the nonsuppressed and the suppressed mode; in both cases the NO_3^- ions are absorbing species (Fig. 4), and (2) the Cl^-, HPO_4^{2-} and SO_4^{2-} ions yielded responses of opposite signs in the nonsuppressed and the suppressed mode (Figs. 1—3). In the nonsuppressed mode the Cl^-, HPO_4^{2-} and SO_4^{2-} ions gave negative UV-detector responses, i. e. when the portion of the eluent containing these ions passed through the detector, a negative (less absorbing) signal was obtained. On the other hand, when the suppressed (dual-column) mode was applied these ions (Cl^-, HPO_4^{2-} and SO_4^{2-}) yielded positive detector responses (as absorbing species). The negative responses to Cl^-, HPO_4^{2-} and SO_4^{2-} show that aqueous solutions of NaCl, Na_2HPO_4 and Na_2SO_4 are more transparent than the eluent (4 mM Na_2CO_3 aqueous solution).

The UV-detector responses (Figs. 1—4) may be compared to the absorbances and molar extinction coefficients of the corresponding solutions, measured with a spectrophotometer in which the stray light level is much lower than that in the chromatographic UV-detector used (see Figs. 5—11). This comparison has led us to the conclusion that the diminishing of the UV-detector responses (Figs. 1—3) at the shortest wavelengths is solely a stray light effect and has nothing to do with the absorption of the respective solutions. Nevertheless, the information presented in Figs. 1—4 seems to be useful to researchers applying chromatographic UV-detectors based on unsophisticated optical systems. The sample and reference solutions used in absorbance and extinction coefficient measurements with the spectrophotometer were chosen as similar to the solutions applied in chromatographic experiments as possible.
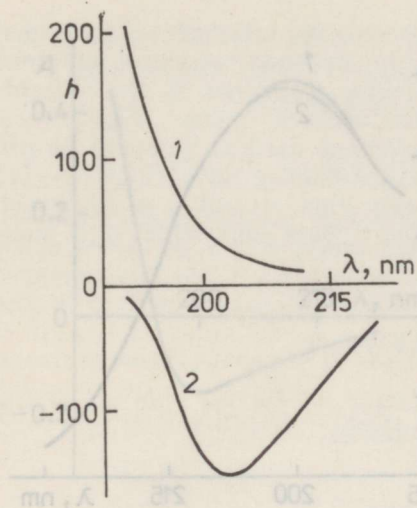
Fig. 1. UV-detector response to Cl⁻ ions. *1* — suppressed carbonate eluent (0.43 g Na₂CO₃/l); *2* — nonsuppressed carbonate eluent (0.43 g Na₂CO₃/l). The ordinate is the peak height, mm, of 200 ppm NaCl solution injected with a 0.43 ml loop. The settings used: 0.16 AUFS and 200 mV/full scale.
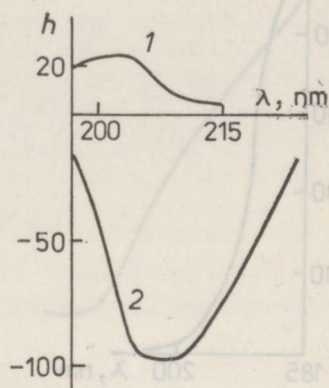

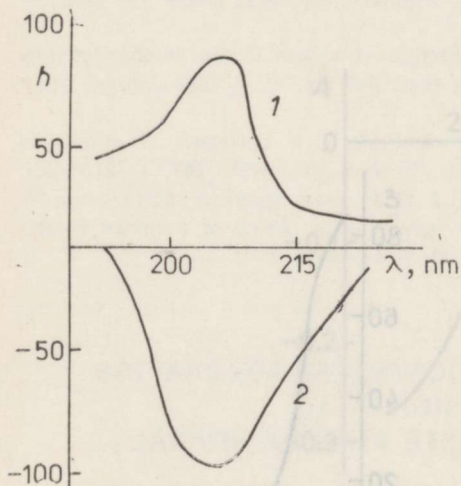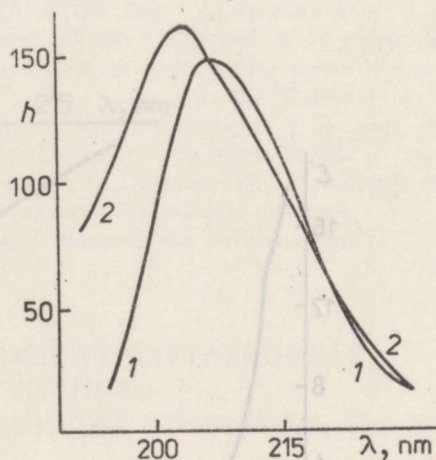Fig. 2. UV-detector response to HPO_4^{2-} ions. *1* — suppressed cabronate eluent (0.43 g Na₂CO₃/l); *2* — nonsuppressed carbonate eluent (0.43 g Na₂CO₃/l). The ordinate is the peak height, mm, of 200 ppm HPO_4^{2-} solution injected with a 0.43 ml loop. The settings used: 0.16 AUFS and 100 mV/FS.

Fig. 3. UV-detector response to SO_4^{2-} ions. *1* — suppressed carbonate eluent (0.43 g Na₂CO₃/l); *2* — nonsuppressed carbonate eluent (0.43 g Na₂CO₃/l). The ordinate is the peak height, mm, of 151 ppm SO_4^{2-} solution injected with a 0.43 ml loop. The settings used: 0.16 AUFS and 100 mV/FS.

Fig. 4. UV-detector response to NO_3^- ions. *1* — suppressed carbonate eluent (0.43 g Na₂CO₃/l); *2* — nonsuppressed carbonate eluent (0.43 g Na₂CO₃/l). The ordinate is the peak height, mm, of 12.5 ppm NO_3^- solution injected with a 0.43 ml loop. The settings used: 0.16 AUFS and 500 mV/FS.
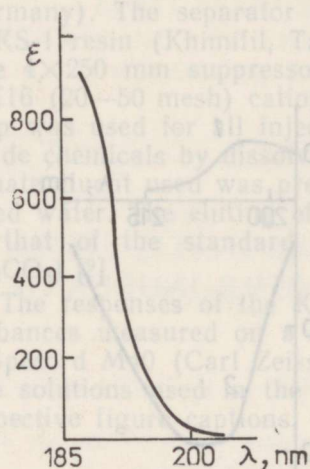
1*

Fig. 5. Molar extinction coefficient of Cl⁻ ions in water vs. wavelengths. The sample cell was filled with 1.22 mM NaCl aqueous solution; the reference cell, with distilled water.
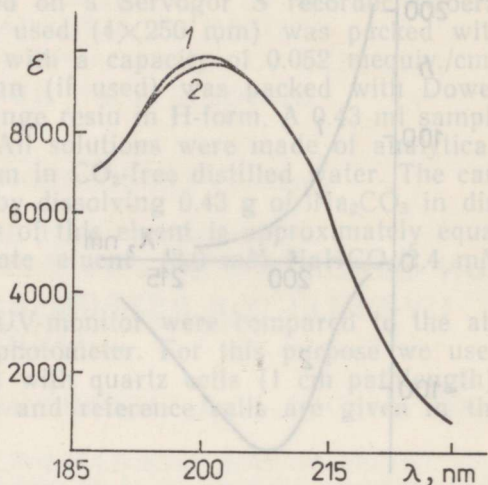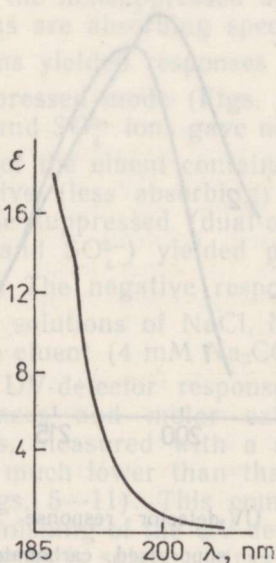
Fig. 6. Molar extinction coefficient of NO_3^- ions vs. wavelengths. 1 — in water, the sample cell was filled with aqueous NaNO₃ solution (0.10 mM) and the reference cell, with distilled water; 2 — in eluent (0.43 g Na₂CO₃/l), the sample cell was filled with the eluent containing also 0.154 mM NaNO₃ and the reference cell, with pure eluent.

In the last case the eluent was converted into a water solution containing 4 mM H₂CO₃. The UV-detector responses to the ions studied may be divided into two groups: (1) the NO_3^- ions yielded a positive response in both the nonsuppressed and the suppressed mode; in both cases NO_3^- ions are absorbing species (Fig. 4), and (2) the Cl⁻, HPO_4^{2-} and SO_4^{2-} ions yielded responses of opposite signs in the nonsuppressed and the suppressed mode (Figs. 1—3). In the nonsuppressed mode the Cl⁻, HPO_4^{2-} and SO_4^{2-} ions gave negative UV-detector responses, i.e. when the portion of the eluent containing these ions passed through the detector, a negative (less absorbing) signal was acquired. On the other hand, when the suppressed (dual column) mode... these ions (Cl⁻, HPO_4^{2-} and SO_4^{2-}) yielded positive detector responses (as absorbing species). The negative responses to Cl⁻, HPO_4^{2-} and SO_4^{2-} show that aqueous solutions of NaCl, Na₂HPO₄ and Na₂SO₄ are more transparent than the eluent (4 mM Na₂CO₃ aqueous solution).

Fig. 7. Molar extinction coefficient of HPO_4^{2-} ions vs. wavelengths. The sample cell was filled with 44.4 mM NaH₂PO₄ aqueous solution; the reference cell, with distilled water.
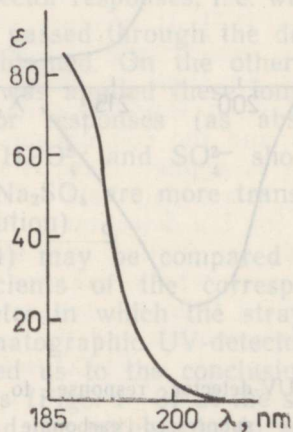
Fig. 8. Molar extinction coefficient of SO_4^{2-} ions vs. wavelengths. The sample cell was filled with 10.4 mM Na₂SO₄ aqueous solution; the reference cell, with distilled water.
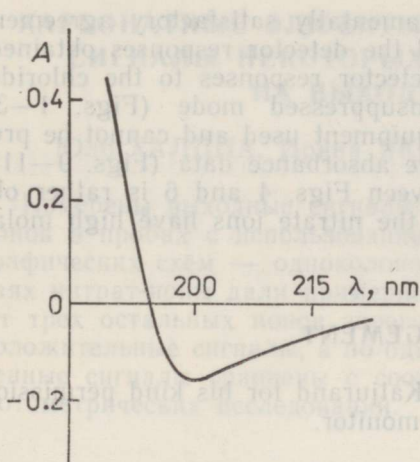
Fig. 9. Absorbance, A, of Cl^- ions in the eluent (0.43 g Na_2CO_3/l) after the separator column. The sample cell was filled with the mixture of 3.44 mM (200 ppm) $NaCl + 2.39$ mM Na_2CO_3, i.e. the total $C_{Na^+} = 8.22$ mM. The reference cell was filled with 4.08 mM Na_2CO_3, i.e. the total $C_{Na^+} = 8.16$ mM.

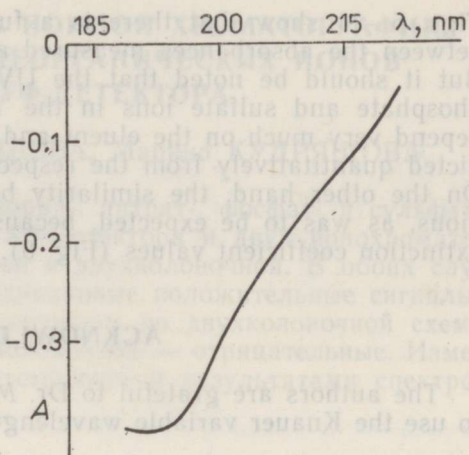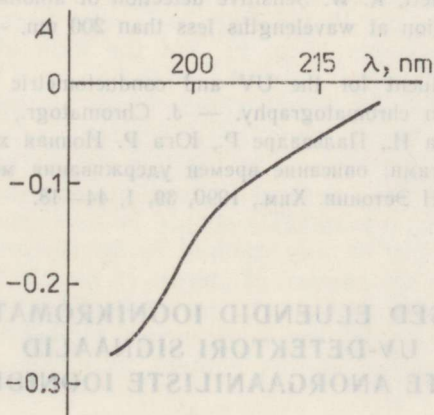Fig. 10. Absorbance, A, of HPO_4^{2-} ions in the eluent (0.43 g Na_2CO_3/l) vs. wavelengths. The sample cell was filled with 2.12 mM NaH_2PO_4 (200 ppm HPO_4^{2-}) + 3.05 mM Na_2CO_3, the total $C_{Na^+} = 8.22$ mM. The reference cell was filled with pure eluent (0.43 g Na_2CO_3/4.08 mM Na_2CO_3), total $C_{Na^+} = 8.16$ mM.

Fig. 11. Absorbance, A, of SO_4^{2-} ions in the eluent (0.43 g Na_2CO_3/l) after the separator column. The sample cell was filled with 1.57 mM Na_2SO_4 (151 ppm SO_4^{2-}) + 2.54 mM Na_2CO_3, the total $C_{Na^+} = 8.22$ mM. The reference cell was filled with pure eluent (0.43 g Na_2CO_3/l), the total $C_{Na^+} = 8.16$ mM.

Figs. 5—11 show that there is a fundamentally satisfactory agreement between the absorbances measured and the detector responses obtained. But it should be noted that the UV-detector responses to the chloride, phosphate and sulfate ions in the nonsuppressed mode (Figs. 1—3) depend very much on the eluent and equipment used and cannot be predicted quantitatively from the respective absorbance data (Figs. 9—11). On the other hand, the similarity between Figs. 4 and 6 is rather obvious, as was to be expected, because the nitrate ions have high molar extinction coefficient values (Fig. 6).

ACKNOWLEDGEMENT

REFERENCES

1. Haddad, P. R. and Jackson, P. E. Ion Chromatography. Elsevier, Amsterdam, 1990.
2. Frankenberger, W. T., Mehra, H. C. and Gjerde, D. T. Environmental applications of ion chromatography. — J. Chromatogr., 1990, **504**, 2, 211—245.
3. Williams, R. J. Determination of inorganic anions by ion chromatography with ultraviolet absorbance. — Anal. Chem., 1983, **55**, 851—855.
4. Small, H., Stevens, T. S., Bauman, W. Novel ion exchange chromatographic method using conductometric detection. — Anal. Chem., 1975, **47**, 11, 1801—1809.
5. MacDonald, J. C. Determination of inorganic anions by ultraviolet absorbance detection. — Am. Lab., 1979, **11**, 45—55.
6. Gerritse, R. G. and Adeney, J. A. Rapid determination in water of chloride, sulphate, sulphite, selenite, selenate and arsenate among other inorganic and organic solutes by ion chromatography with UV detection below 195 mm. — J. Chromatogr., 1985, **347**, 3, 419—428.
7. Ayers, G. P. and Gillett, R. W. Sensitive detection of anions in ion chromatography using UV detection at wavelengths less than 200 nm. — J. Chromatogr., 1984, **284**, 2, 501—514.
8. Ivey, J. P. Novel eluent for the UV and conductometric detection of anions in unsuppressed ion chromatography. — J. Chromatogr., 1983, **267**, 1, 218—221.
9. Халдна Ю., Яковлева И., Пальвадре Р., Юга Р. Ионная хроматография с карбонатными элюентами: описание времен удерживания методом главных компонент. — Изв. АН Эстонии. Хим., 1990, **39**, 1, 44—48.

KARBONAATSED ELUENDID IOONIKROMATOGRAAFIAS. UV-DETEKTORI SIGNAALID MÕNINGATE ANORGAANILISTE IOONIDE KORRAL

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On mõõdetud UV-detektori väljundsignaale, kui analüüsitavas proovis leidus Cl^--, NO_3^--, HPO_4^{2-}- ja SO_4^{2-}-ioone. Sealjuures on ioonikromatograafias kasutatud nii ühe kolonni kui ka kahe kolonni skeeme. Nitraatioonide puhul täheldati mõlema skeemi kasutamisel enam-vähem ühesuguseid positiivseid UV-detektori signaale. Teiste uuritud ioonide puhul saadi kahe kolonni skeemi kasutades positiivsed ning ühe kolonni skeemi kasutades negatiivsed UV-detektori signaalid. Mõõdetud signaale on võrreldud vastavate spektrofotomeetriliste mõõtmiste tulemustega.

КАРБОНАТНЫЕ ЭЛЮЕНТЫ В ИОННОЙ ХРОМАТОГРАФИИ. СИГНАЛЫ НЕКОТОРЫХ НЕОРГАНИЧЕСКИХ ИОНОВ НА ВЫХОДЕ УФ-ДЕТЕКТОРА

Юло ХАЛДНА, Ирина ЯКОВЛЕВА, Марина КУДРЯШОВА

Измерены выходные сигналы хлорид-, нитрат-, фосфат- и сульфат-ионов в пробах с использованием УФ-детектора и двух ионохроматографических схем — одноколоночной и двухколоночной. В обоих случаях нитрат-ионы дали примерно одинаковые положительные сигналы. От трех остальных ионов зарегистрированы по двухколоночной схеме положительные сигналы, а по одноколоночной — отрицательные. Измеренные сигналы сравнены с соответствующими результатами спектрофотометрических исследований.