

All-Solid-State Ion-Selective Electrodes Based on Graphite Paste for Determination of Calcium(II) and Nitrate

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Abstract

Robust and easy-to-handle ion-selective electrodes in all-solid-state configurations based on graphite paste have been developed for applications in environmental samples. The electrode consists of different functional layers (graphite paste, conducting polymer, ion-selective membrane). The ion-selective compounds have been incorporated in polyvinylchloride (PVC) membranes. Polypyrrole (PPy) acts as a solid contact and an intermediate layer between the ion-selective membrane and the graphite paste. As ion-complexing compounds tridodecylmethylammonium nitrate (TDMA-NO₃) for nitrate, N,N,N',N'-tetra[cyclohexyl]diglycolic acid diamide and N,N-dicyclohexyl-N',N'-dioctadecyl-diglycolic diamide for calcium(II) determinations have been used. The electrodes have been tested in drinking and well water samples by direct potentiometric determination and by titrations. The results have been compared to ion chromatography as the reference method. Both ion selective electrodes exhibit linear response from 10⁻⁵ mol/L to 10⁻¹ mol/L respectively. The detection limits for the target ions are below 10⁻⁶ mol/L based on the respective ion.

Keywords: all-solid-state configuration, ion-selective electrode, drinking water, potentiometric titration, ion chromatography

1. Introduction

There is a great demand for mobile and in-field usable analyzers for ion analysis. Inexpensive, simple and fast chemical sensors should be used to check whether the level of an analyte is below or above the highest allowed concentration.

Laboratory based instrumental analysis methods like ion chromatography and atomic absorption spectrometry are not usable in field and require expensive equipment and qualified personnel. Electrochemical methods have the advantages of high sensitivity and selectivity, simplicity and low cost. Ion-selective electrodes in all-solid-state configuration without any liquid components can be used in an advantageous manner in field for potentiometric ion analysis due to their high sensitivity, simple construction form and good functionality. Conventional ion-selective electrodes consist of an internal reference electrode, which contains an inner liquid electrolyte and therefore are not suitable in field. In-field usable, easy-to-handle chemical analyzers are needed.

Since the discovery of graphite paste electrodes for electroanalytical applications by Adam, they have attracted much attention due to their advantages such as ease of preparation, stable response, and loss of internal electrolyte (Svancara, Kalcher, Walcarius, & Vytras, 2012; Bobacka, Ivaska, & Lewenstam, 2008; Radu et al., 2013). Development of all-solid-state ion-selective electrodes for determination of environmental important ions is of great interest in many application fields (Wang, Chou, & Liu, 2003; Abramova, Moral-Vico, Soley, Ocana, & Bratov, 2016; Enseleit et al., 2018; Yin, Li, & Qin, 2017; Bomar, Owens, & Murray, 2017; Wardek, 2014).

Instrumental laboratory analysis methods like ion chromatography and atomic absorption spectrometry require expensive and sophisticated equipment as well as laboratory-based infrastructure. Chemicals of high purity and qualified personnel are also needed. These analysis methods are not suitable for field analysis.

There is still a great need for ion determination of different ions in many different applications. Determination of calcium(II) as an important parameter for water hardness is needed in many different fields of water analysis. High nitrate contamination in ground, well and surface water has become a serious problem in Germany. The limiting value

for nitrate in drinking water in the European Community is 50 mg/L. Reduction of use of fertilizers is in discussion in order to reduce the nitrate entry in the environment. For both target ions user-friendly analyzers for field and continuous on-line determinations in real samples are needed in different application fields.

In this work we report on preparation, potentiometric characterization and analytical applications of new inexpensive, miniaturized, simple, robust and field-usable all-solid-state ion-selective electrodes based on graphite paste for nitrate and calcium(II) determinations in drinking water samples. The electrodes are characterized by thin functional polymeric layers and therefore allow an easy and reproducible electrode preparation.

2. Experimental

2.1 Reagents and Materials

All reagents were analytical grade and used without any further purification. All inorganic salts used were purchased from Sigma-Aldrich. All aqueous solutions were prepared with deionized water with a conductivity of 0.055 $\mu\text{S}/\text{cm}$. As ion complexing compounds) N,N,N',N'-tetra[cyclohexyl]diglycolic acid diamide, N,N-dicyclohexyl-N',N'-dioctadecyl-diglycolic diamide and TDMA-NO₃ have been used. As plasticizers 2-nitrophenyloctyl ether and dibutyl phthalate have been used. Reagent grade, high molecular weight poly(vinyl chloride) (PVC), tetrahydrofuran, ethylene diaminetetraacetic acid disodium salt dihydrate, potassium tetrakis (4-chloro-phenyl)borate and pyrrole were purchased from Sigma Aldrich. Plasticizers, ion complexing compounds, of the highest purity were available and used without further purification. As eluents for ion chromatographic anion detection Na₂CO₃ (3.6 mmol/L) and for cation detection HNO₃ (1.7 mmol/L) and dipicolinic acid (0.7 mmol/L) have been used.

2.2 Apparatus and Reference Electrodes

Potentiometric measurements were carried out at room temperature using pH/ion analyzer pMX 3000 and a laboratory measuring system LM 2000 with software LM remote from Xylem Analytics Germany Sales GmbH & Co. KG Sensortechnik, Meinsberg. Ag/AgCl reference electrodes (Kurt-Schwabe-Institut) with saturated KCl electrolyte have been used. An ion chromatography system (IC 850 Metrohm, Switzerland) has been used for the reference analysis.

3. Results and Discussion

3.1 Electrode Preparation

The ion-selective all-solid-state electrodes consist of following different functional layers:

- First layer: graphite paste (mixture of graphite powder and resin).
- Second layer: polypyrrole (PPy) as conducting polymer.
- Third layer: ion-selective (polyvinyl) chloride membrane.

All layers are incorporated in an electrode plastic body and adhere well on the corresponding substrate. PPy is deposited onto graphite paste surface by electropolymerization of pyrrole. The PVC based membranes were prepared by dissolving of the ion-complexing compound together with the plasticizer, the PVC and the additive in tetrahydrofuran. PPy acts as a solid contact and intermediate layer between the ion-selective membrane and the graphite paste. It replaces the internal liquid electrolyte of conventional ion-selective electrodes. The ion-selective cocktail with the immobilized ion-complexing compound is then drop-casted onto the PPy-layer. Electrode preparation and optimized membrane composition are described elsewhere (Schwarz, Trommer, & Mertig, 2016; Schwarz, Trommer, & Mertig, 2018; Schwarz, Trommer, Gerlach, & Mertig, 2018).

Figure 1 shows a photograph (a) and a schematic view with the functional layers (b) of a miniaturized ion-selective electrode in all-solid-state configuration.

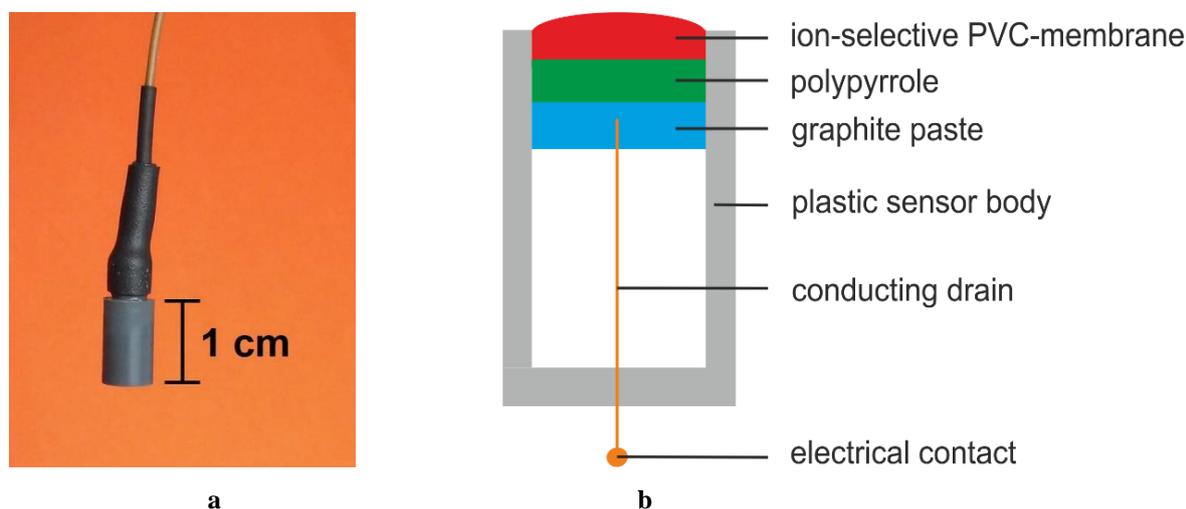


Figure 1. Photography (a) and schematic view (b) of an ion-selective, all-solid-state electrode

Commercially available ion-complexing reagents for target ions are used and shown in Table 1. For preparation of calcium(II)-selective electrodes both diamides have been used and show comparable response behavior.

Table 1. Membrane compositions

membrane component	Calcium(II)-selective electrode	Nitrate-selective electrode
ionophore	<i>a)</i> <i>N,N,N',N'</i> -tetra[cyclohexyl]diglycolic acid diamide <i>b)</i> <i>N,N</i> -dicyclohexyl- <i>N',N'</i> -dioctadecyl-diglycolic diamide	tridodecylmethylammonium nitrate
plasticizer	2-nitrophenyl octyl ether	dibutyl phthalate
polymer	poly(vinyl chloride)	poly(vinyl chloride)
additive	potassium tetrakis(4chlorophenyl)-borate	---

3.2 Calcium(II)-Selective All-Solid-State Electrodes

The response behavior of calcium(II)-selective electrodes in standard and real samples including the corresponding calibration curve are shown in Figure 2. The electrodes were conditioned before measurements for 12 h in 10^{-3} mol/L CaCl_2 solution.

The relative standard deviation (RSD) for calcium(II) determinations in the concentration range of 10^{-3} mol/L till 10^{-5} mol/L was below 5 % (n= 9).

As real samples different drinking water samples have been investigated. After calibration in standard solutions, the electrodes were washed with deionized water, and then immersed in the target sample. The electrodes show stable potentials in standard and real samples. Following calcium(II) contents for different drinking water samples were evaluated by direct potentiometry with the new ion-selective electrodes:

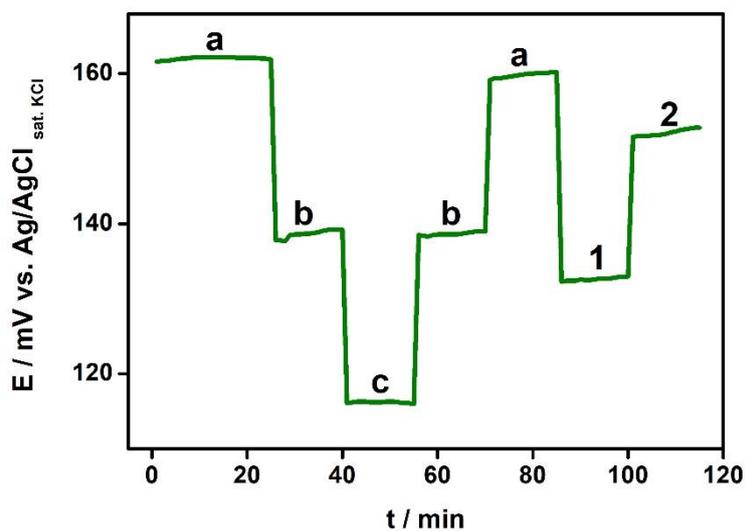
- sample 1 (drinking water from Freiberg, Germany): 23 mg/L,
- sample 2 (drinking water from Lützensnitz, Germany): 129 mg/L.

Figure 3 shows the ion chromatogram of sample 1. Reference analysis by ion chromatography yielded a calcium(II) amount of 29 mg/L.

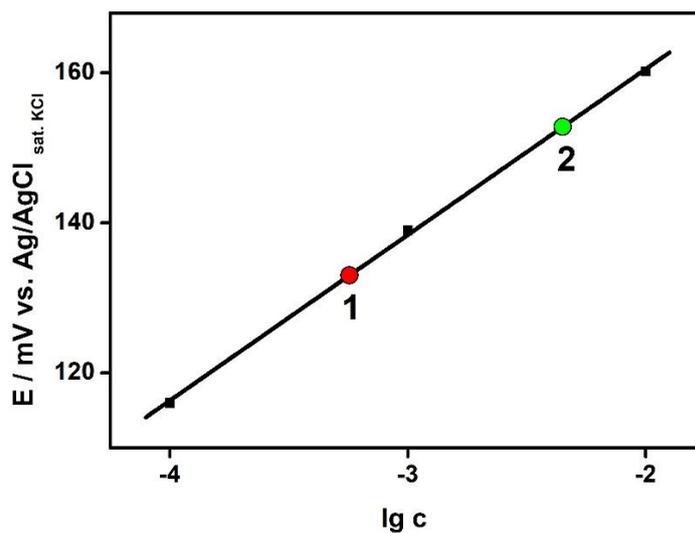
Figure 4 shows a potentiometric titration curve (a) and the first derivative (b) of a drinking water sample (Karsdorf, Germany) with the new calcium(II)-selective electrode. The drinking water samples have been adjusted to pH 12 by adding NaOH (2 mol/L). The calcium(II) amount obtained by titration using new calcium(II)-selective electrode yielded 35 mg/L. The titration curve shows a sharp and significant potential jump which could be used successfully for analytical applications.

In figure 5 a chromatogram of a drinking water sample (Karsdorf, Germany) is illustrated. The obtained calcium(II)

value by ion chromatography was 38 mg/L. The reference analysis was carried out by titration using calcon carbon acid as color indicator revealed a calcium(II) amount of 35 mg/L. Thus, the results obtained by different analysis methods show good accordance.



a



b

Figure 2. Response behavior (a) and corresponding calibration curve (b) of a calcium(II)-selective electrode in standard and real samples; CaSO_4 standards: a: 10^{-2} mol/L, b: 10^{-3} mol/L, c: 10^{-4} mol/L; sample 1: drinking water (Freiberg, Germany), sample 2: drinking water (Lützenschnitz, Germany)

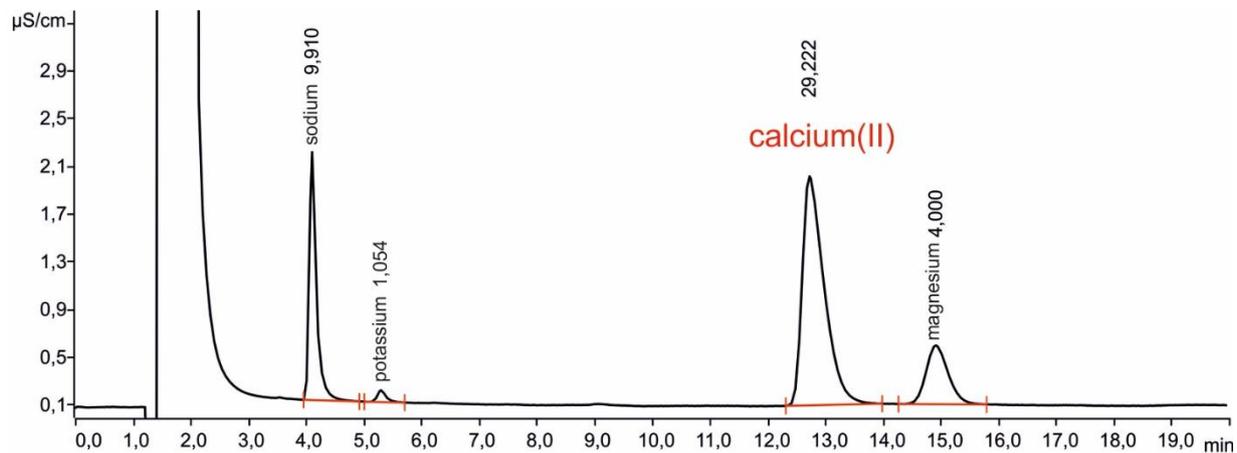
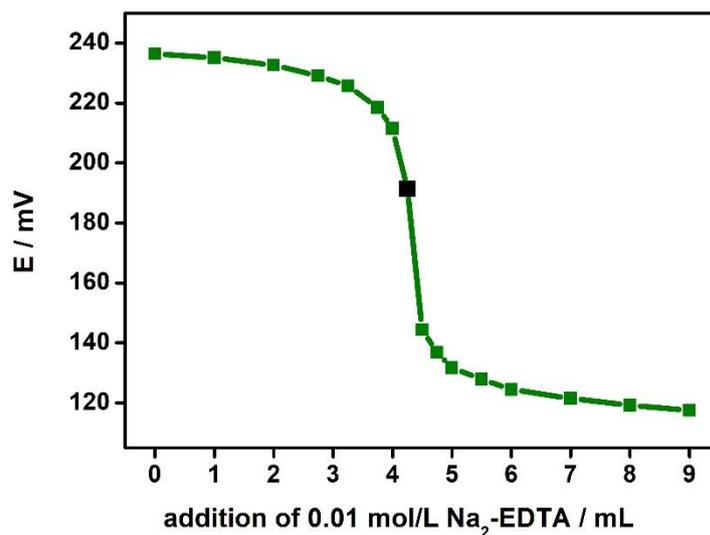
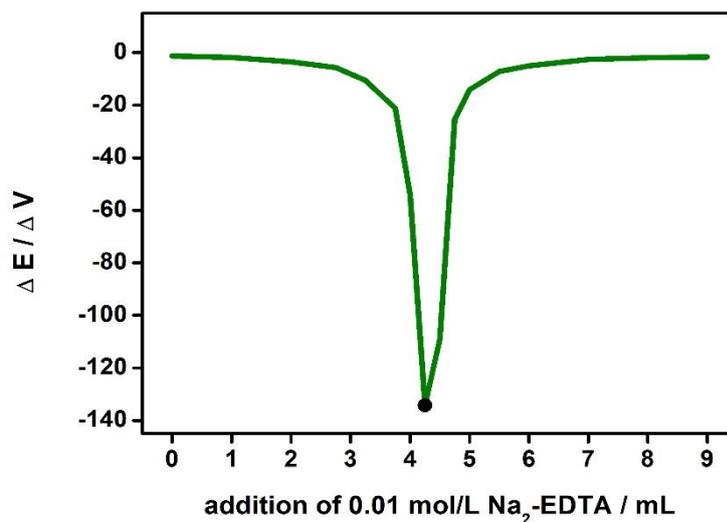


Figure 3. Chromatogram of a drinking water sample (Freiberg, Germany)



a



b

Figure 4. Titration curve (a) and first derivative (b) of a drinking water sample (Karsdorf, Germany)

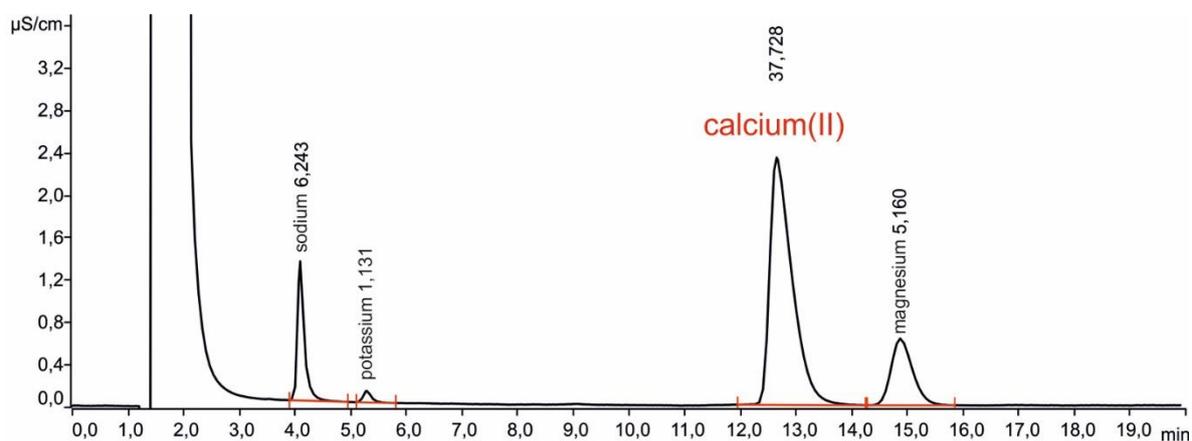


Figure 5. Chromatogram of a drinking water sample (Karsdorf, Germany)

The calcium(II)-selective electrodes show sensitivities in the linear range (10^{-5} mol/L - 10^{-1} mol/L) of >25 mV/decade in average. The results obtained by potentiometry with new calcium(II)-selective electrodes show good accordance to results of ion chromatography.

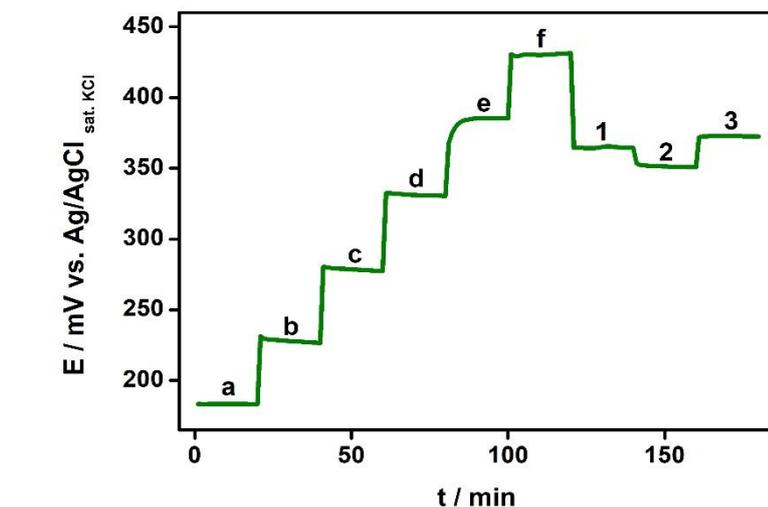
3.3 Nitrate-Selective All-Solid-State Electrodes

Figure 6 shows the response behavior of a nitrate-selective electrode in standard and different drinking water samples, as well as the corresponding calibration curve. Following nitrate concentrations in the samples have been determined by direct potentiometry using the new nitrate electrodes. In brackets, values obtained by ion chromatography are shown. The results of the different analysis methods agree well.

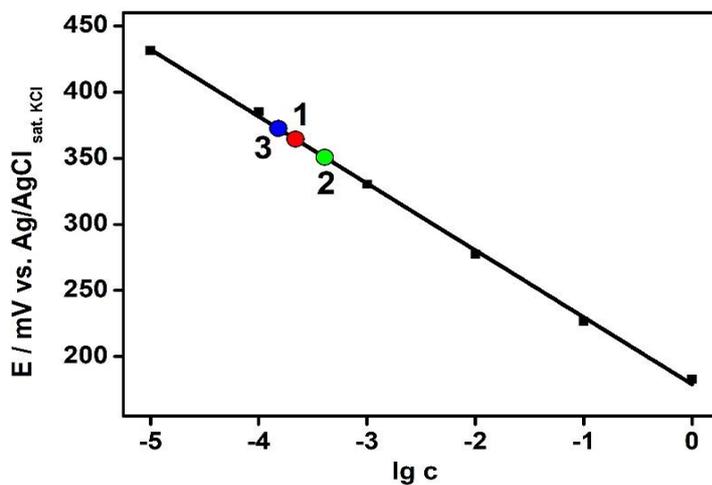
- sample 1 (drinking water from Freiberg, Germany): 14 mg/L (15 mg/L),
- sample 2 (drinking water from Döbeln, Germany): 25 mg/L (23 mg/L),
- sample 3 (drinking water from Chemnitz, Germany): 9 mg/L (10 mg/L).

In Figure 7 a chromatogram of a drinking water sample is shown. The comparison of results well justifies the potential of these electrodes for direct potentiometric nitrate determination in drinking water samples without any addition of chemicals and sample preparation.

In the concentration range 10^{-5} mol/L till 10^{-1} mol/L the nitrate-selective electrode exhibited linear Nernstian potential response. The average sensitivity is > -55 mV/decade. A selectivity coefficient of -1.6 for chloride as the main interfering ion was evaluated after the fixed interference method. The relative standard deviation (RSD) for nitrate determination in the concentration range of 10^{-3} mol/L till 10^{-1} mol/L was below 4 % ($n = 5$). The electrodes can be used in the pH-range of 3-9.



a



b

Figure 6. Response behavior (a) and calibration curve (b) of a nitrate-selective electrode in standard and real samples; NH_4NO_3 standards a 1 mol/L, b 10^{-1} mol/L, c 10^{-2} mol/L, d 10^{-3} mol/L, e 10^{-4} mol/L, f 10^{-5} mol/L; drinking water samples: 1 Freiberg, 2 Döbeln, 3 Chemnitz

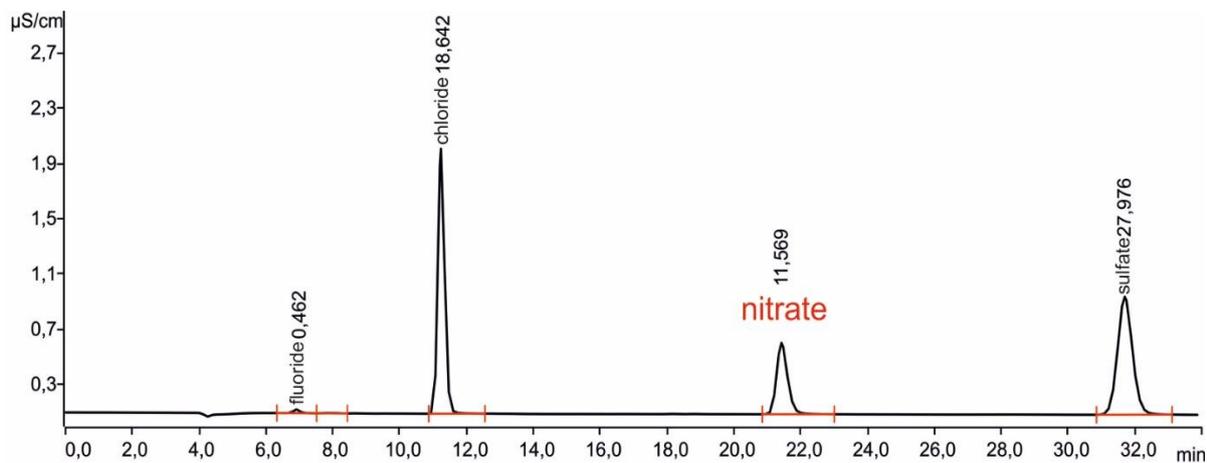


Figure 7. Chromatogram of a drinking water sample (Freiberg, Germany)

4. Conclusions

The new solid-contact, ion-selective electrodes based on graphite paste show remarkable stable and reproducible potentials. They are characterized by simple construction and all-solid-state configuration. Both electrodes provide a Nernstian response for both target ions in the linear range. The conducting polymer polypyrrole acts as a solid contact, replacing the inner electrolyte solution. Results obtained by potentiometric ion determinations using the new ion-selective electrodes are comparable with results obtained from ion chromatography. In most cases a good consistency between these different analytical methods is achieved. Both electrodes can be used successfully in drinking water analysis using direct potentiometry. The calcium(II)-selective electrodes also show good results in potentiometric titrations of tap water samples. The new developed all-solid-state ion-selective electrodes are particularly attractive for mobile and decentralized ion analysis due to their low cost, simple instrumentation, loss of liquid electrolyte and high durability. Furthermore, they are miniaturizable and easy-to-handle. Experiments concerning long-term behavior under real environmental conditions in field and under the influence of different interfering ions will be carried out in future.

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