

Luminescent Sensor for Carbonate Ion Based on Lanthanide (III) Complexes of 1,4,7,10-Tetraazacyclododecane-1,4,7-Triacetic Acid (DO3A)

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Abstract Lanthanide(III) complexes of 1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid (H_3DO3A) are suggested as sensors for sensitive luminescence-based determination of a carbonate anion. Thermodynamic study of association of $[Eu(H_2O)_2(DO3A)]$ with bidentate anionic ligands using luminescence spectroscopy reveals an affinity order $CO_3^{2-} > oxalate^{2-} > picolinate^- > phthalate^{2-} \approx citrate^{3-}$; presumably as a consequence of an increasing chelate ring size. The ternary $[Eu(DO3A)(picolinate)]^-$ and $[Tb(DO3A)(picolinate)]^-$ complexes show improved photophysical properties due to the antenna effect of the picolinate anion. High quenching effect of carbonate anion and, to a lesser extent also oxalate, enables construction of a linear calibration plot utilizing optimized experimental conditions (e.g. $c_{LnL} = 0.1$ mM, $c_{picolinate} = 2-5$ mM, $pH = 7.4$, $\lambda_{exc} = 286$ nm, etc.) for carbonate determination in solution. Both sensors show a comparable sensitivity and the detection limit of about 0.4 mM. In order to

improve the photophysical properties of Ln(III) sensor by shift of excitation wavelength about 40 nm to VIS range, the isoquinoline-3-carboxylic acid (IQCA) as antenna ligand was employed instead of picolinic acid. The analysis of commercial samples of European mineral waters was carried out and they were compared to the results obtained by capillary isotachopheresis to confirm there is no inherent (systematic) error to the present analysis. The Ln(III) sensor with IQCA is recommended since it has a better robustness than that with picolinate. The present analytical method is simple and rapid, and it is useful for sensitive determination of bicarbonate/carbonate concentration in water samples under aerobic conditions.

Keywords Luminescent probe · Anions · Carbonate · Lanthanide complexes · DOTA derivative · Speciation monitoring

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Introduction

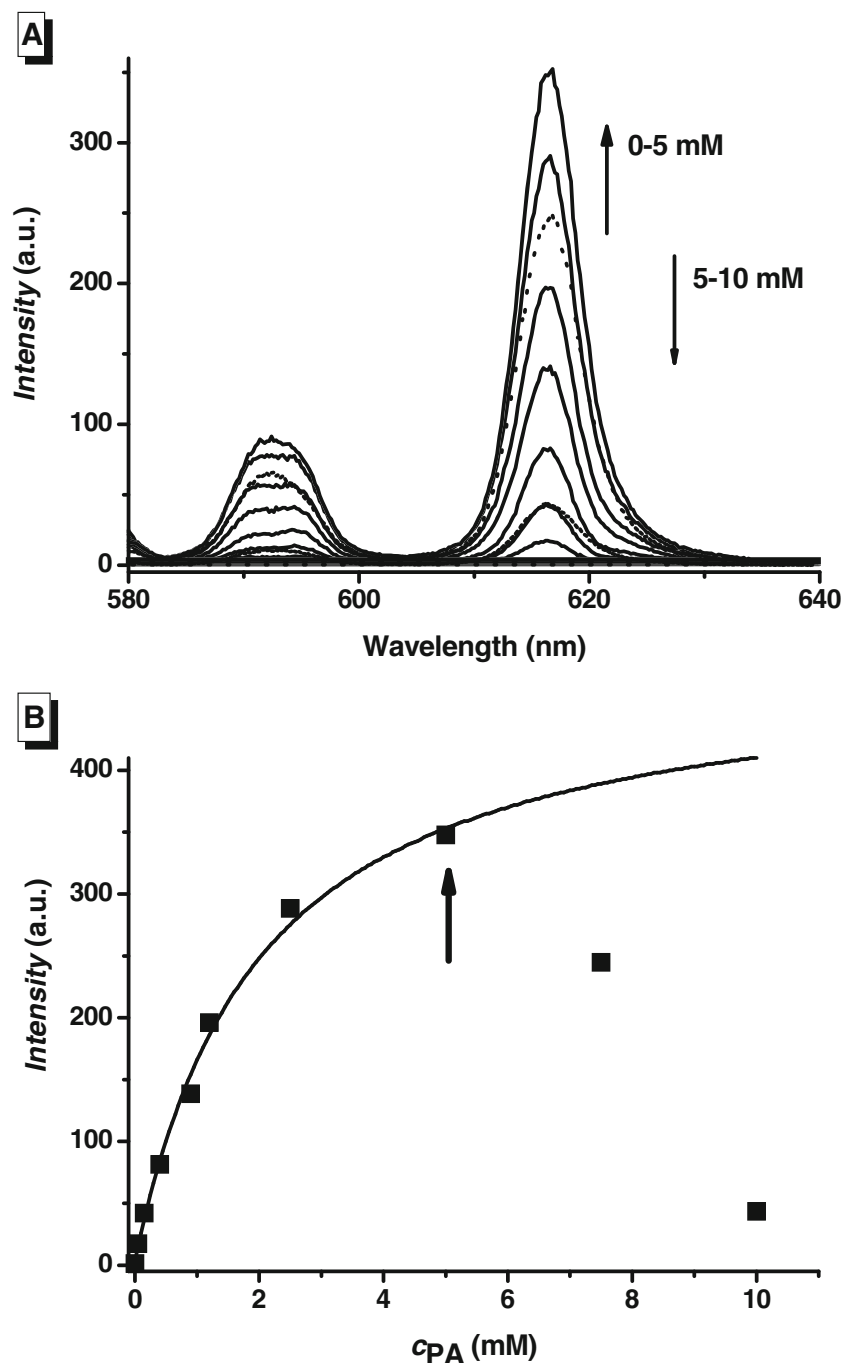
Lanthanide(III) complexes of macrocyclic ligands, for example DOTA derivatives, are used as radiopharmaceuticals (^{90}Y , ^{153}Sm , ^{166}Ho , ^{177}Lu) [1–3] or MRI contrast agents (Gd) [4] in medicine or as luminescent probes (Eu, Tb in VIS and Yb, Nd in NIR regions) [5–8]. The Eu(III) and Tb(III) complexes display rather unusual luminescence properties, including a large Stokes shift with emission at wavelength above 450 nm, narrow luminescence bands with half-widths being 10–20 nm and luminescence lifetimes up to hundreds of microseconds) [9, 10].

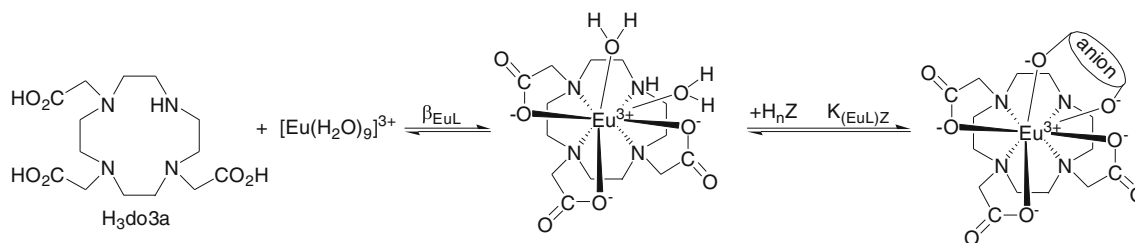
The 1,4,7,10-tetraazacyclododecane-1,7-diacetic acid (H_2DO2A) and 1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid (H_3DO3A) are hexa- and heptadentate macrocyclic ligands that yield very stable complexes with europium(III) ion [11, 12]. Both complexes also form ternary lanthanide(III)-containing species with both mono- and bidentate ligands. Examples of

such ternary complexes are Ln(III)-H₂DO₂A-fluoride, -acetate or -hydrogenphosphate [13], Ln(III)-H₂DO₂A-dipicolinate [14, 15], Ln(III)-H₃DO₃A-hydrogenphosphate, or bicarbonate [16]. Thus, the binary complexes of the Ln(III)-H₂DO₂A and Ln(III)-H₃DO₃A may be employed for determination of anions known to form the ternary complexes as given above. The antenna effect, in which the Eu(III) luminescence is sensitized by a fluorophore such as dipicolinic acid, can also be used for sensitive determination of an analyte capable of sensitizing the Eu(III) luminescence. For example, [Ln(H₂O)₃(DO₂A)]⁺ serves as a probe for dipicolinic acid, which is an anthrax-related

pathogenic marker [14, 15], a Ln(III) complex of DO₃A-triamide ligand can be used for determination of salicylic acid and its derivatives [17], or they can work as logic gates [8]. On the other hand, the ternary complex can be also used as a sensor, e.g. ternary complex formed from an Ln(III)-DO₃A-triamide derivative and β -diketone or Ln(III) complex of DO₃A-triamide with attached fluorophore have been used for determination of acetate, bicarbonate or lactate [5, 6, 18–20]. More examples of anion sensors and other sensors have been reviewed [21–23] and the methods used for development of anion sensors have been given elsewhere [7, 8].

Fig. 1 a Emission spectra of [Eu(H₂O)₂(DO₃A)] complex in the presence of different concentration of picolinic acid (PA) ($c_{\text{EuL}}=0.1$ mM, pH=7.4, $\lambda_{\text{exc}}=286$ nm). The dotted spectrum was obtained for a solution having higher concentration of picolinic acid ($c_{\text{PA}} > 5$ mM). **b** Plot of luminescence intensity of the Eu(III)-H₃DO₃A-PA system at 616 nm as a function of the PA concentration (the experimental data disturbed by the self-quenching of the free PA were ignored during evaluation of stability constant of the ternary complex; behind the arrow)





Scheme 1 The formation of the ternary $[\text{Eu}(\text{DO3A})(\text{Z})]^{n-}$ complexes; Z^{n-} = ligand anions as given in Table 1 (carbonate $^{2-}$, picolinate $^{-}$, oxalate $^{2-}$, citrate $^{3-}$, phthalate $^{2-}$, isoquinoline-3-carboxylate $^{-}$), $\text{L} = \text{DO3A}^{3-}$

Here, we report on the formation of ternary Eu(III) and Tb(III) complexes with macrocyclic ligands and important bioanalytes (citrate, carbonate, oxalate anions) investigated by luminescence spectroscopy. Selective anionic sensors suitable for carbonate anion determination based on the $[\text{Ln}(\text{H}_2\text{O})_2(\text{DO3A})]$ complexes are demonstrated, and their advantages over the prior carbonate sensors are described [24, 25]. The results shown here suggest a potential utility of this sensor for a construction of differential sensor arrays [26].

Experimental

Materials and Reagents

Potassium salts of phosphate, oxalate, 5-sulfosalicylate, citrate, phthalate, sodium bicarbonate and picolinic acid = PA

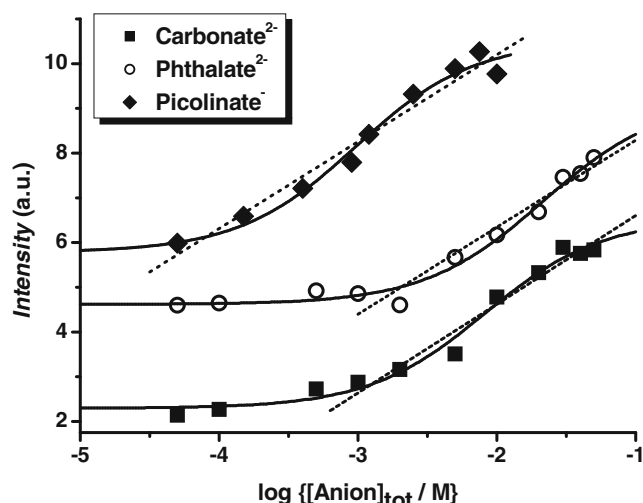


Fig. 2 Examples of experimental luminescence data used for the evaluation of stability constants of the ternary complexes ($\lambda_{\text{exc}} = 394$ nm; for PA: $c_{\text{EuL}} = 0.1$ mM, $\text{pH} = 7.4$, $I = 0.1$ M; for other anions: $c_{\text{EuL}} = 1.0$ mM, $\text{pH} = 7.2$, $I = 0.5$ M). The data were fitted with parameters given in Table 1 (solid line). The dotted line shows the linear dependence in the range of anion concentrations suitable for a possible determination of anion concentrations. The experimental points for formation of the ternary $[\text{Eu}(\text{DO3A})(\text{picolinate})]^{-}$ complex were increased by 5 a.u. for the sake of clarity

(all p.a. grade, Sigma-Aldrich, USA) and isoquinoline-3-carboxylic acid = IQCA (Acros Organics, Belgium) were used as received. The macrocyclic ligand, $\text{H}_3\text{DO3A} \cdot \text{H}_2\text{SO}_4$, was a kind gift of Bracco SpA, Italy. Stock solutions of $\text{Eu}(\text{ClO}_4)_3$, EuCl_3 or TbCl_3 were prepared by dissolving Eu_2O_3 or Tb_4O_7 (p.a., Alfa, Germany) in a small excess of perchloric or hydrochloric acid and were standardized by chelatometric titration. Ionic strength was adjusted to 0.1 or 0.5 mol dm^{-3} by KCl. All measurements were carried out at 25.0 ± 0.5 °C.

Instrumentation

Determination of bicarbonate/carbonate by capillary isotachopheresis (CITP) was carried out on one-column EA 102 electrophoretic analyzer (Villa Labeco, Spišská Nová Ves, Slovakia) at room temperature using PTFE capillary (diameter 0.3 mm, length 90 mm) connected to a conductivity detector. The analyte concentrations (injected as 30 μl of analyzed solution) were determined in the following system: 10 mM HCl + 20 mM imidazole (leading electrolyte, $\text{pH} = 7.0$), 100 mM boric acid (terminating electrolyte, $\text{pH} = 8.0$) at constant current 50 μA . The standard addition method was employed to determine the

Table 1 The equilibrium constants for formation of the ternary complexes in the $\text{Eu}(\text{III})\text{-H}_3\text{DO3A}\text{-anion}$ systems as determined by luminescent spectroscopy

Ligand, Z (log $K_{p,i}$)	Log ($^{\text{cond}}K_{(\text{EuL})\text{Z}}$)	Log ($K_{(\text{EuL})\text{Z}}$) ^c	Luminescence enhancement ^f
$(\text{CO}_3)^{2-}$ (9.61, 6.00)	$2.03 \pm 0.14^{\text{ac}}$	$4.55 \pm 0.11^{\text{ac}}$	2.86
$(\text{oxalate})^{2-}$ (3.65, 1.10)	$3.87 \pm 0.27^{\text{ac}}$	$3.87 \pm 0.27^{\text{ac}}$	12.04
$(\text{picolinate})^{-}$ (5.21, 0.95)	$2.84 \pm 0.06^{\text{bcd}}$	$2.84 \pm 0.06^{\text{bcd}}$	7.10^{c} , 170.1^{d}
$(\text{citrate})^{3-}$ (5.30, 4.14, 2.80)	$1.75 \pm 0.16^{\text{ac}}$	$1.75 \pm 0.16^{\text{ac}}$	2.75
$(\text{phthalate})^{2-}$ (4.65, 2.66)	$1.68 \pm 0.14^{\text{ac}}$	$1.68 \pm 0.14^{\text{ac}}$	2.00

Conditional constants $^{\text{cond}}K_{(\text{EuL})\text{Z}}$ at ^a $\text{pH} = 7.2$, $I = 0.5$ M KCl and ^b $\text{pH} = 7.4$, $I = 0.1$ M KCl

^c $\lambda_{\text{exc}} = 394$ nm

^d $\lambda_{\text{exc}} = 286$ nm

^e $K_{(\text{EuL})\text{Z}} = [\text{EuLZ}]/\{[\text{EuL}] \times [\text{Z}]\}$

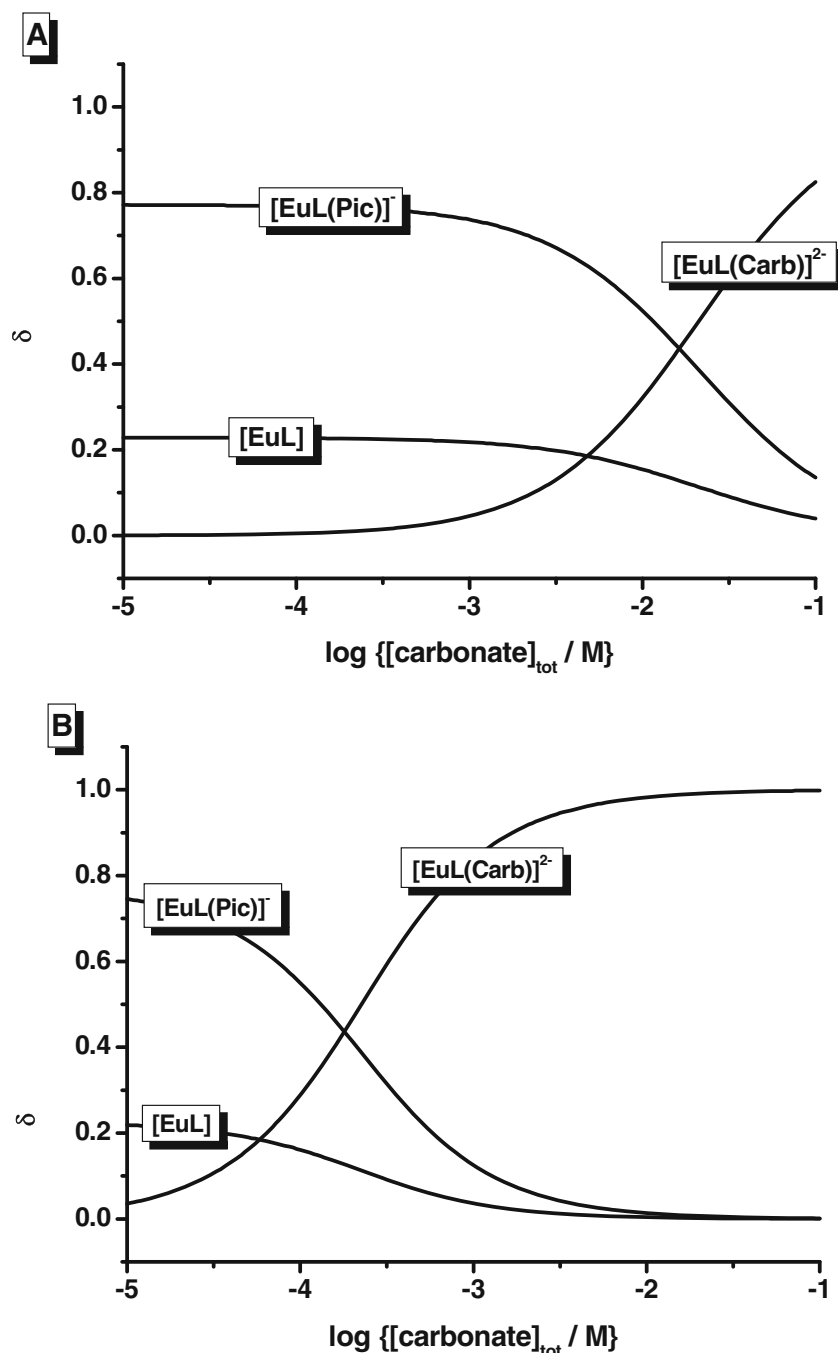
^f $I(\text{EuLZ})/I(\text{EuL})$

solubility of atmospheric CO_2 (as the bicarbonate species) in distilled water in pH region 7–8 and the resulting data were used as a blank in the analysis. All measurements performed by CITP were repeated at least three times for each concentration level. The bicarbonate analysis in European mineral waters was performed without sample pretreatment, the sample was only diluted 10-times (CITP) or 3–10-times (luminescence) prior the analysis depending on bicarbonate content in the sample.

All luminescence spectra including life-time measurements and 3D spectral maps were recorded on spectrometer

Aminco-Bowman Series 2 (Thermo-Spectronic, U.S.A.) operating with continuous or flash Xe-lamp in wavelength range 200–800 nm. Stock solution of the $[\text{Eu}(\text{H}_2\text{O})_2(\text{DO3A})]$ complex was prepared by mixing Eu (III) salt and ligand (in a slight excess) solutions at pH 5.5 and the resulting solution was left at room temperature for least 24 h prior the measurements. The formation of the ternary complex is fast therefore the luminescence-based analysis was performed by mixing the $[\text{Eu}(\text{H}_2\text{O})_2(\text{DO3A})]$ complex solution with the particular anion solution (see experimental details in Figs. 1

Fig. 3 The simulated distribution diagrams using equilibrium constants given in Table 1 for pH=7.4 (a) and pH=10.0 (b). Other concentrations are: $c_{\text{EuL}} = 0.1 \text{ mM}$, $c_{\text{PA}} = 5 \text{ mM}$. Legend to diagrams: L = $(\text{DO3A})^{3-}$, Pic = $(\text{picolinate})^-$, Carb = $(\text{carbonate})^{2-}$



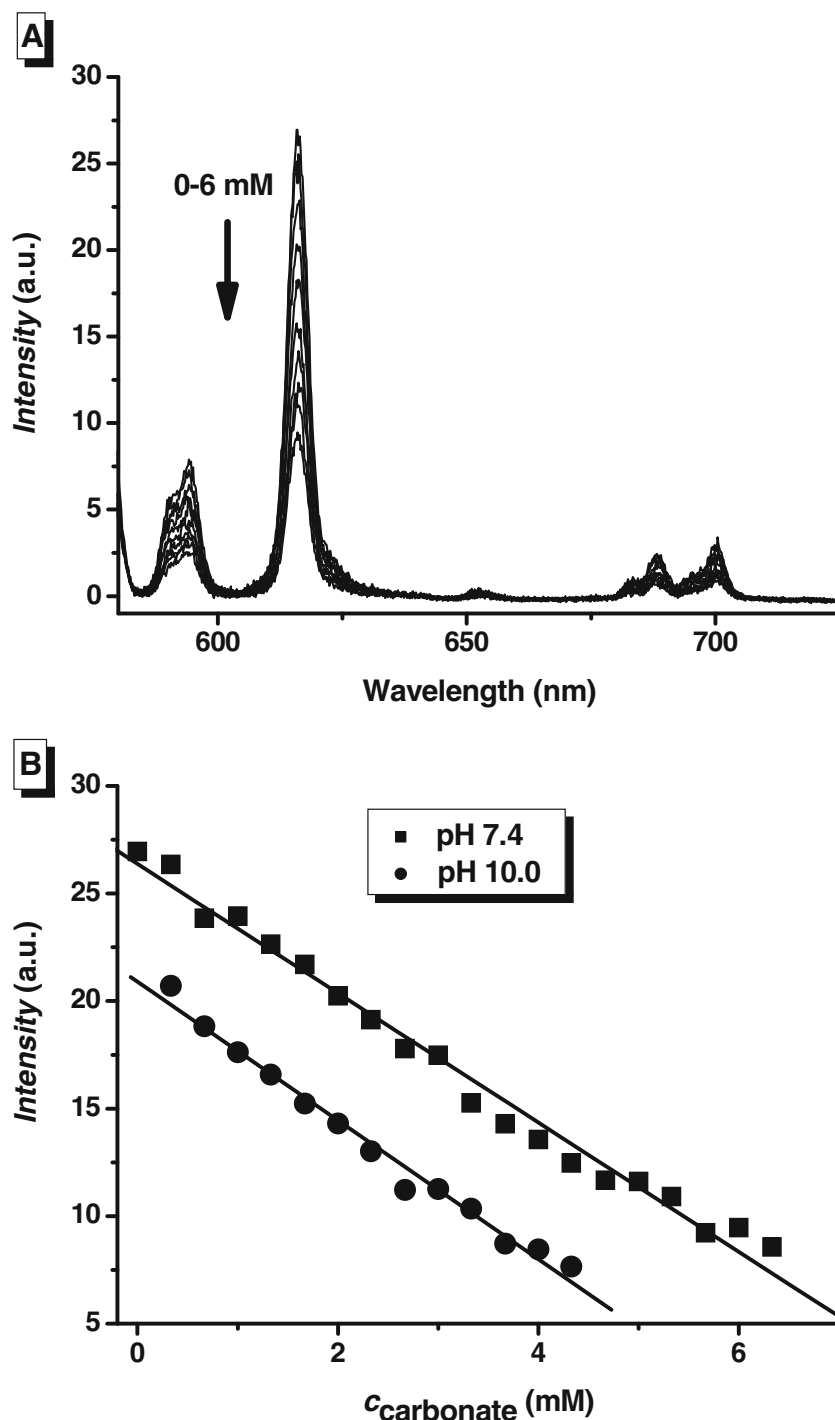
and 2) and the luminescence data were recorded after equilibrating the sample for 5 min at temperature 25.0 ± 0.5 °C. The baseline corrected output data were treated by OPIUM program [27, 28] to get stability constants of the ternary species. The analytical procedures for luminescence determination of carbonate anions were done under the optimized experimental conditions described in the following chapter.

Results and Discussion

Thermodynamic Study of Formation of Ternary Species

The luminescence properties of the Eu(III)-H₃DO3A complex and its derivatives were recently described [12, 29, 30]. It was found that Eu(III) luminescence lifetime of an Eu(III)-aqua ion (108 μs) is significantly increased in the Eu

Fig. 4 **a** The emission spectra of the ternary [Eu(DO3A)(picolinate)]⁻ complex at different carbonate concentrations ($c_{\text{EuL}}=0.1$ mM, $c_{\text{PA}}=5$ mM, pH=7.4, $\lambda_{\text{exc}}=286$ nm). **b** Plot of luminescence intensity of the [Eu(DO3A)(picolinate)]⁻ complex at 616 nm as function of carbonate concentration



(III)-DO3A complex (290 μs) [16], and up to 400 μs in other complexes of similar nature [29]. From these data, two water molecules were estimated to be coordinated to Eu(III) ion in the Eu(III)-DO3A complex (see Scheme 1) [12, 16, 29]. Replacement of these coordinated water molecules with bidentate anions leads to the formation of $[\text{Eu}(\text{DO3A})(\text{anion})]^{n-}$ ($n=1,2$) ternary species (Scheme 1).

The formation thermodynamics of the ternary Eu(III)-containing species was followed by luminescence spectroscopy (Figs. 1 and 2). Formation of the ternary Eu(III) complexes during titration experiment (Fig. 1) is accompanied by an increase of luminescence intensity as two water molecules are being displaced from the first coordination shell by the bidentate ligand (Scheme 1). This phenomenon has been previously observed by time-resolved luminescence spectroscopy during binding carbonate to the $[\text{Eu}(\text{H}_2\text{O})_2(\text{DO3A})]$ complex resulting in an increase of luminescence lifetime from 290 μs for the Eu(III)-DO3A complex to 499 μs for the ternary species [16].

The luminescence spectra recorded as function of the bidentate ligand concentration (Fig. 2) were used to determine conditional stability constants $^{\text{cond}}K_{(\text{EuL})\text{Z}}$ (Table 1). These values were used to calculate thermodynamic stability constants $K_{(\text{EuL})\text{Z}}$ (stepwise constant, Scheme 1) using known protonation constants ($K_{\text{p},i}$) of the ligands taken from the literature [16, 31]. The results are shown in Table 1. There is only one conditional constant, $\log(^{\text{cond}}K_{(\text{EuL})\text{Z}}) \sim 1.5$ (pH 7.5, $I=0.15$ M), in literature for the ternary carbonate species [16]. Our measurement resulted in a similar value of the conditional constant, $\log(^{\text{cond}}K_{(\text{EuL})\text{Z}}) \sim 2.0$ (pH 7.2, $I=0.5$ M); the difference can be caused by different experimental conditions as pH and ionic strength. Thermodynamic stability constant of a carbonate adduct with Eu(III) complex of a ditopic ligand derived from DO3A-triamide was recently published to have value of $\log K_{(\text{EuL})\text{Z}}=4.8$ [32].

The values of thermodynamic constant for formation of the ternary species (Table 1) decrease in the order: $(\text{CO}_3)^{2-} > (\text{oxalate})^{2-} > (\text{picolinate})^- < (\text{phthalate})^{2-} \approx (\text{citrate})^{3-}$. This fact might be connected with differences in conformation, size and/or overall basicity of the anions. The highest stability of the carbonate ternary complex might be due to the highest basicity of the carbonate and small sterical hindrances caused by formation of the four-membered chelate ring with the smallest anion. Oxalate or picolinate anions (forming five-membered chelate ring) are less sterically demanding than the remaining anions (forming six/seven-membered rings); the oxalate is the smallest one in the organic anion series. Using the selective excitation of Eu(III) ion in complex (394 nm), the luminescence is 2–12 fold enhanced due to formation of the ternary complex. It is explained as a consequence of elimination of the vibrational quenching through O–H bonds of the coordinated water

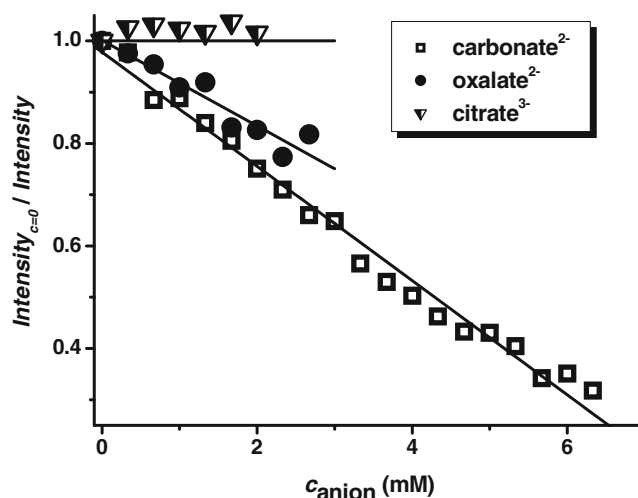


Fig. 5 The normalized (see plot in Fig. 4) calibration plot for luminescent determination of anions ($c_{\text{EuL}}=0.1$ mM, $c_{\text{PA}}=5$ mM, pH=7.4, $\lambda_{\text{exc}}=286$ nm, $\lambda_{\text{em}}=616$ nm), $\text{Intensity}_{c=0}$ and Intensity are analytical signals luminescence of the ternary $[\text{Eu}(\text{DO3A})(\text{picolinate})]^-$ complex in absence and in presence of the anions, respectively

molecules (see Scheme 1) while the increase of luminescence signal as a function of anion concentration (Fig. 2) is approximately linear (in the log scale) with a slope about 2. Due to the relatively low selectivity and sensitivity of this method, the particular calibration plot ($S = f(c_{\text{anion}})$) can be used for analytical purposes only in simple cases. In the case when the analyte coordinated to the lanthanide(III) ion can sensitize the lanthanide(III) emission [33–36] due to its antenna effect, as it is the case of the picolinate anion, the resulting ternary complex can yield a higher luminescence enhancement. Excitation of Eu(III) through the picolinate absorption band at $\lambda_{\text{exc}}=286$ nm yields 170-times

Table 2 The metrological parameters of the analytical methods discussed in text

Method	Complex used as sensor, pH	Sensitivity, M^{-1} ^d Limit of detection, mM
Luminescence	$[\text{Eu}(\text{H}_2\text{O})_2(\text{DO3A})]$, 7.4 ^a	(114±3) 0.3 ₂
Luminescence	$[\text{Eu}(\text{H}_2\text{O})_2(\text{DO3A})]$, 10.0 ^a	(160±7) 0.3 ₆
Luminescence	$[\text{Tb}(\text{H}_2\text{O})_2(\text{DO3A})]$, 7.4 ^b	(106±3) 0.2 ₈
Luminescence	$[\text{Tb}(\text{H}_2\text{O})_2(\text{DO3A})]$, 10.0 ^b	(150±8) 0.4 ₃
Capillary isotachopheresis (CITP)	– ^c	(3.97±0.1 ₈)×10 ^{4c} 0.4 ₂

^a $\lambda_{\text{em}}=616$ nm

^b $\lambda_{\text{em}}=546$ nm

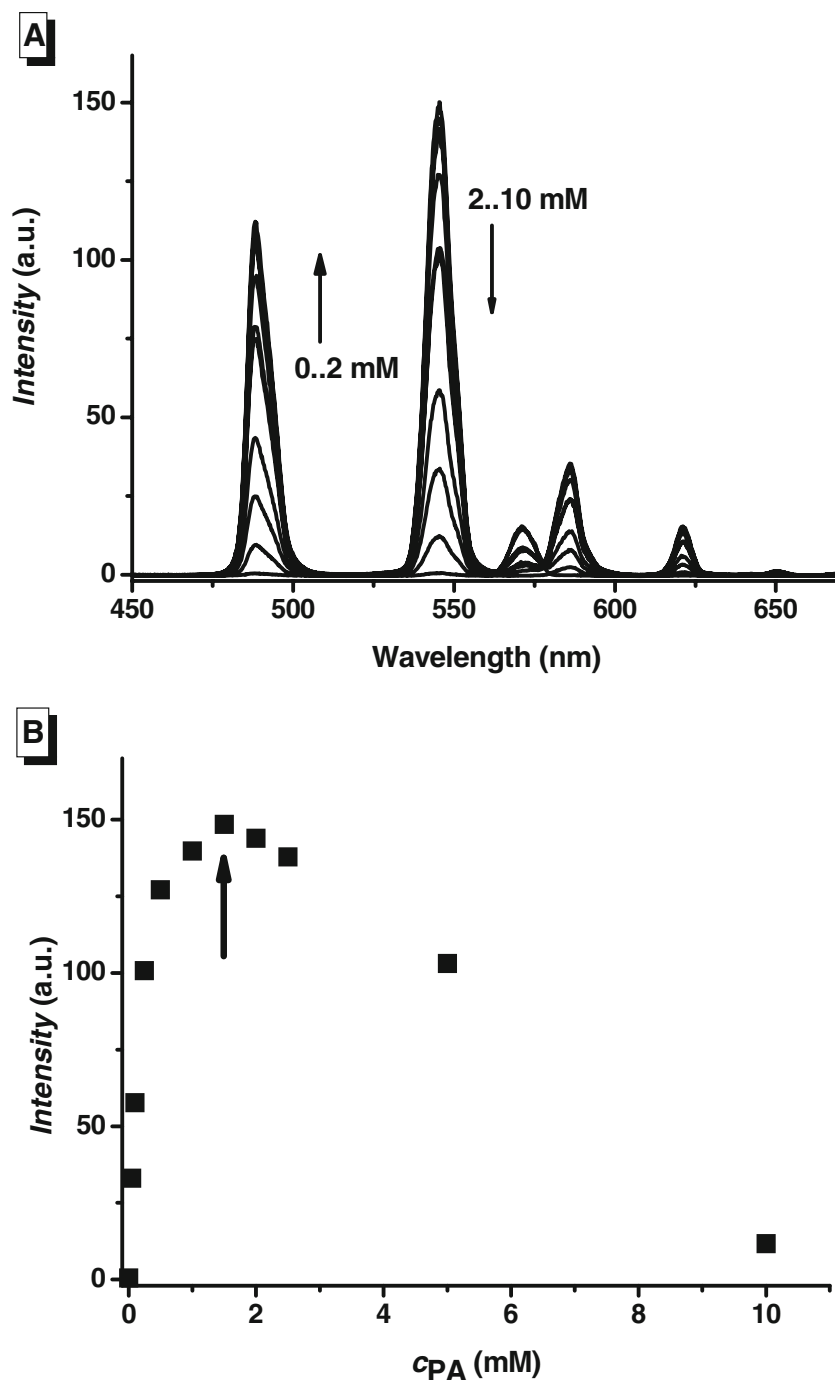
^c Details are given in Experimental Section

^d Calculated from luminescence experimental data after normalization (see Fig. 5)

^e Sensitivity is given in “ s M^{-1} ”

higher luminescence intensity of the corresponding picolinate ternary complex compared to the starting $[\text{Eu}(\text{H}_2\text{O})_2(\text{DO3A})]$ complex (Fig. 1 and Table 1). However, at higher concentration of the free PA in the solution, a quenching effect on luminescence of the ternary complex was observed. The increase of luminescence intensity of ternary $[\text{Eu}(\text{DO3A})(\text{picolinate})]^-$ complex corresponds to the higher quantum yield as observed for an analogous $[\text{Eu}(\text{H}_2\text{O})(\text{DO3A-pyNox})]$ complex ($\text{H}_3\text{DO3A-pyNox}$ = triacetic acid-(2-methylene-pyridine-N-oxide) analog of H_4DOTA) [37].

Fig. 6 **a** Emission spectra of the $[\text{Tb}(\text{H}_2\text{O})_2(\text{DO3A})]$ complex after addition of PA ($c_{\text{TbL}}=0.1$ mM, $\text{pH}=7.4$, $\lambda_{\text{exc}}=286$ nm). **b** Plot of luminescence intensity of Tb (III) complex at 546 nm as function of PA concentration. The luminescence of the ternary complex is self-quenched at higher PA concentrations



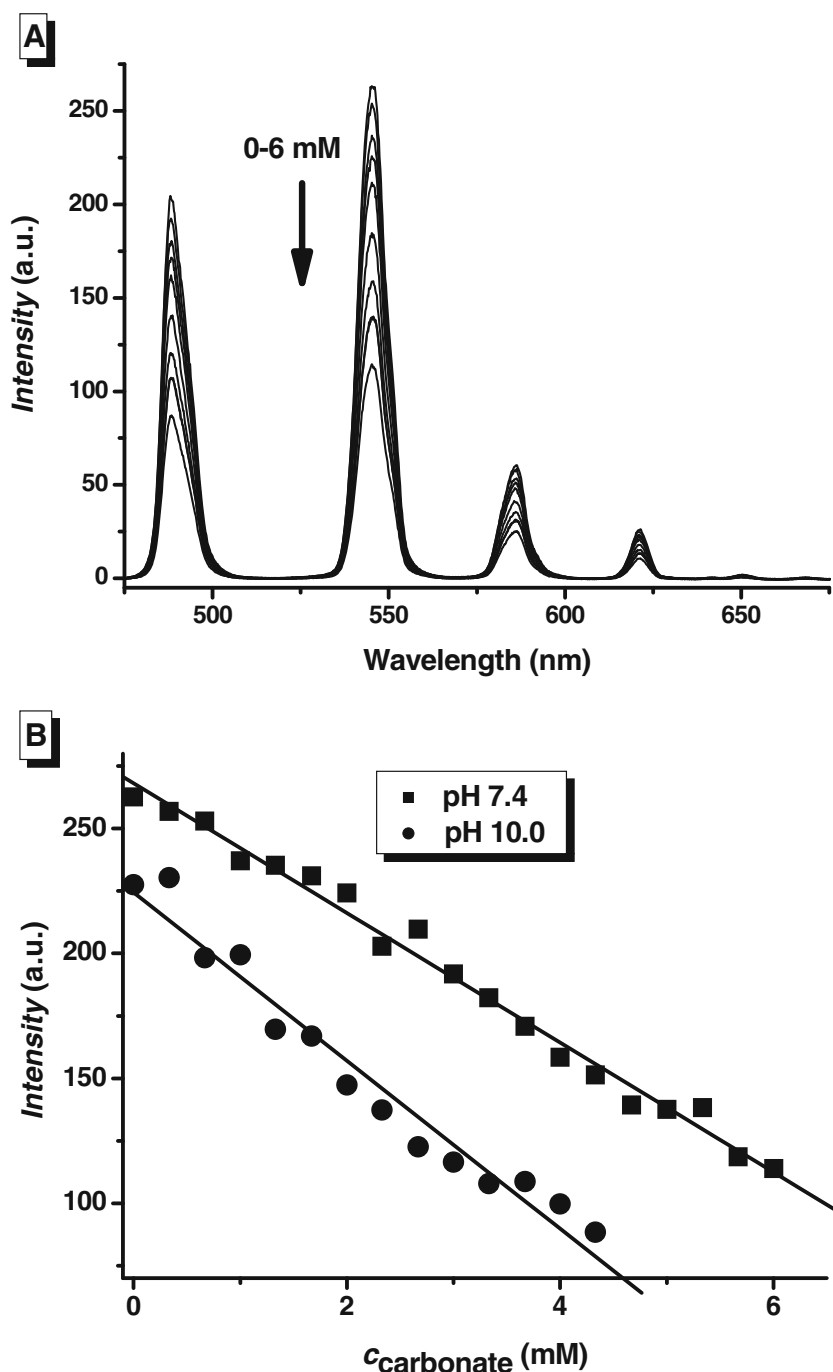
Development of Sensor

The experimental data described above prompted us to utilize the ternary $[\text{Eu}(\text{DO3A})(\text{picolinate})]^-$ complex as a potential practically useful sensor using substitution of picolinate by anion species forming more stable ternary complex (see Table 1). In order to optimize experimental conditions for this sensor, distribution diagrams for the $\text{Eu}(\text{III})-(\text{DO3A})^{3-}-\text{PA}^-$ carbonate- H^+ system were simulated with the knowledge of all necessary equilibrium constants (Fig. 3). From the

simulation, it can be inferred that PA concentration of 5 mM is necessary to achieve the maximal abundance of the ternary $[\text{Eu}(\text{DO3A})(\text{picolinate})]^-$ complex at both pH 7.4 and 10 (compare Figs. 1 and 3). Then, the highest value of the analytical luminescence signal of the ternary complex is observed which is not yet quenched by a free picolinate anion as seen at its higher concentrations. In the cases when picolinate anion concentration is not sufficient for the formation of the ternary $[\text{Eu}(\text{DO3A})(\text{picolinate})]^-$ complex, the luminescence signal corresponding to the complex is much lower (e.g. 8-

times smaller for the 0.1 mM picolinate solutions if compared with the signal of the 5 mM solution at pH 7.4; Fig. 1). Upon addition of a carbonate to the $[\text{Eu}(\text{DO3A})(\text{picolinate})]^-$ complex solution, a new ternary $[\text{Eu}(\text{DO3A})(\text{CO}_3)]^{2-}$ species is formed. At pH 7.4 and carbonate concentration between 10^{-3} M and 0.1 M, this process leads to a decrease in luminescence intensity (Fig. 4). When the distribution diagram is simulated for higher pH=10.0, the substitution reaction takes place at a lower carbonate concentration, between 10^{-5} and 10^{-3} M due to higher conditional constant at this pH in

Fig. 7 a The emission spectra of the ternary complex $[\text{Tb}(\text{DO3A})(\text{picolinate})]^-$ after addition of carbonate ($c_{\text{TbL}} = 0.1$ mM, $c_{\text{PA}} = 2$ mM, pH=7.4, $\lambda_{\text{exc}} = 286$ nm). **b** Plot of luminescence intensity of the Tb(III) complex at 545 nm as function of carbonate concentration



comparison to pH=7.4 where bicarbonate is a major species under these experimental conditions [38].

To verify previous predictions based on distribution diagrams (Fig. 3), we carried out experiments under these predicted optimal conditions (Fig. 4). As expected, the observed luminescence spectra are decreasing in intensity with added carbonate. The most sensitive is a sharp peak at 616 nm, which is often highly sensitive to the changes in the symmetry of the complex [6, 10–12, 18, 22]. The quenching effect of carbonate is higher than that of oxalate whilst no effect was observed for citrate (Fig. 5). This is likely to be a consequence of the different thermodynamic stability of the respective ternary complexes (Table 1, the third column).

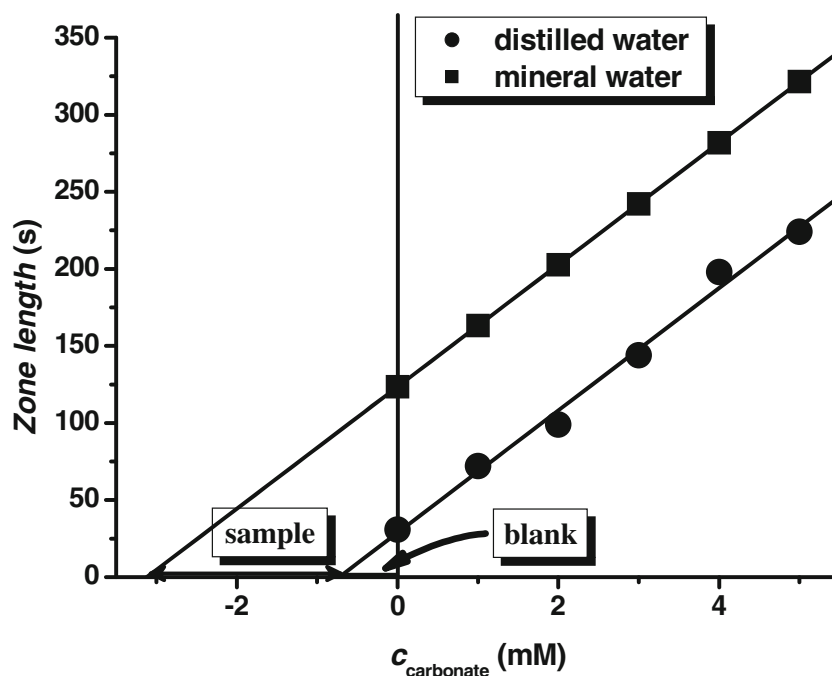
The calibration plot is linear in the millimolar concentration range. Concerning the analytical figures of merit, the method sensitivity is slightly higher at pH 10.0 than at pH 7.4 while the limits of detection (~0.4 mM) are almost the same in both cases (see Table 2). This finding is in contradiction to the results assumed from distribution diagrams (Fig. 3a and b). A possible explanation is the presence and coordination of the hydroxide anion which competes with both picolinate and carbonate anions in the alkaline solutions and leads to formation of the $[\text{Eu}(\text{DO3A})(\text{OH})]^-$ or even $[\text{Eu}(\text{DO3A})(\text{OH})_2]^{2-}$ species [30, 39].

Considering similarity of the analogous complexes, $[\text{Eu}(\text{H}_2\text{O})(\text{DOTA})]^-$ and $[\text{Tb}(\text{H}_2\text{O})(\text{DOTA})]^-$, the thermodynamic stability of the $[\text{Eu}(\text{H}_2\text{O})_2(\text{DO3A})]$ and $[\text{Tb}(\text{H}_2\text{O})_2(\text{DO3A})]$ complexes is expected to be virtually identical [40]. Thus, Tb (III) luminescence can also be employed in the similar applications and the ternary $[\text{Tb}(\text{DO3A})(\text{picolinate})]^-$ complex was

also tested for sensing of a carbonate. The optimal concentration of a picolinate was found to be 2 mM (Fig. 6). Comparing the sensitivity of $[\text{Eu}(\text{DO3A})(\text{picolinate})]^-$ and $[\text{Tb}(\text{DO3A})(\text{picolinate})]^-$ complexes, the both have almost the same values within experimental errors of measurement (Table 2). The same decrease of luminescence intensity after addition of carbonate to the ternary complex solution was observed for both $[\text{Tb}(\text{DO3A})(\text{picolinate})]^-$ and $[\text{Eu}(\text{DO3A})(\text{picolinate})]^-$ complexes (Fig. 7). The most sensitive and sharp emission maximum suitable for the carbonate detection is that at 545 nm. However, the peaks at 488, 586 or 621 nm can also be used. Here, the limit of carbonate detection for both complexes is the same, about 0.4 mM (Table 2).

As a verification of the proposed analytical method, determination of bicarbonate content was performed in a sample of a mineral water brand “Hanácká kyselka” (Czech Republic). CITP was used to confirm the manufacturer’s declared bicarbonate content (25.50 mM). Analysis of air-equilibrated distilled water (Fig. 8) shows concentration of a bicarbonate to be $0.7_2 \pm 0.1_4 \text{ mM}$, i.e. $-\log[\text{HCO}_3^-] = 3.13$. This value is considered as a blank for this analysis and it is in agreement with values found in studies describing the dissolved CO_2 equilibria ($-\log[\text{HCO}_3^-] = 3.33$ at pH=8 as the highest value [24, 38]). The CITP analysis of the mineral water sample found $3.119 \pm 0.003 \text{ mM}$ for a bicarbonate (Fig. 8). The content of bicarbonate in a sample of mineral water corrected for the blank value ($0.7_2 \pm 0.1_4 \text{ mM}$) and the sample dilution was calculated as $23.9 \pm 1.5 \text{ mM}$. Comparison of this value with the manufacturer’s declared content (25.50 mM) using Student *t*-test [41] shows no systematic error in the analysis.

Fig. 8 Example of calibration plot for determination of carbonate in samples of distilled and mineral waters by CITP. The standard addition method was employed

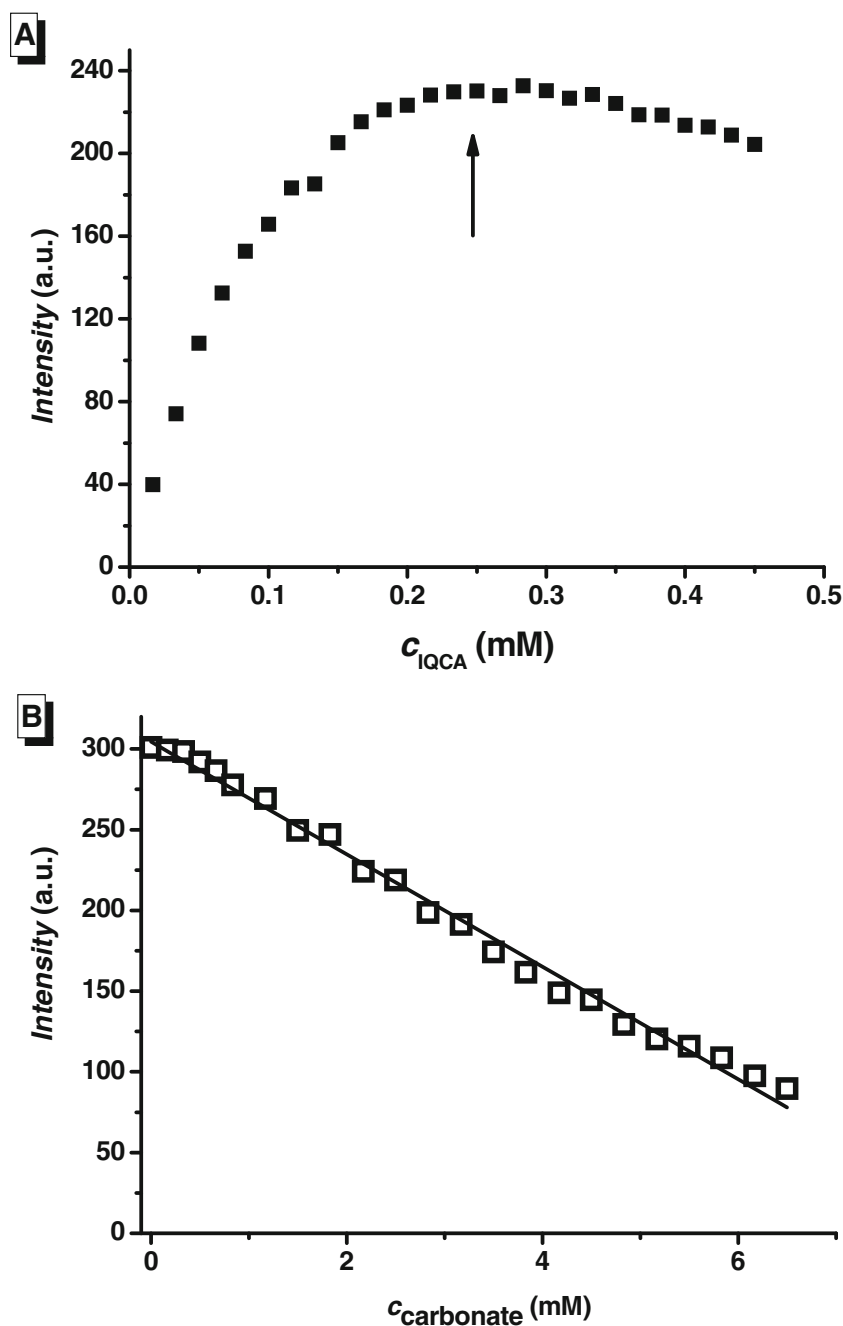


A similar procedure was applied for determination of bicarbonate in the mineral water sample using the above described method utilizing $[\text{Eu}(\text{DO3A})(\text{picolinate})]^-$ or $[\text{Tb}(\text{DO3A})(\text{picolinate})]^-$ complexes as sensors at pH 7.4 (see Figs. 4 and 7). The following the bicarbonate concentrations were estimated as 1.34 ± 0.06 mM and 1.63 ± 0.06 mM, respectively. The blank-corrected bicarbonate concentrations in mineral water were estimated to be 18.6 ± 4.7 mM determined with Eu(III) complex and 27.1 ± 4.7 mM with Tb(III) complex. The higher RSD is likely due to including all possible errors (e.g. high dilution factor, bicarbonate blank concentration due to anaerobic conditions, etc.) as judged

following rules of the error propagation as it has been recommended [41]. The Student *t*-test was used to test for a systematic error in the procedure [41]. This test shows that the procedure with Tb(III) complex used as a sensor is not loaded with systematic error. On the other hand, the procedure with the Eu(III) complex sensor gave systematically underestimated values. However, the luminescence-based analytical determination with the Tb(III) sensor shows similar analytical figures of merit (e.g. sensitivity, limit of detection, etc.) as the procedure using CITP (see Table 2).

Since picolinic acid and its ternary complex absorb in deep UV region (the excitation wavelength is about

Fig. 9 **a** The luminescence intensity of the $[\text{Eu}(\text{H}_2\text{O})_2(\text{DO3A})]$ complex measured at 616 nm after addition of isoquinoline-3-carboxylic acid (IQCA) ($c_{\text{EuL}} = 0.1$ mM, pH=7.4, $\lambda_{\text{exc}} = 326$ nm). **b** Plot of luminescence intensity of the Eu(III)- $\text{H}_3\text{DO3A}$ -IQCA system at 616 nm as a function of carbonate concentration measured under the optimal experimental conditions ($c_{\text{EuL}} = 0.1$ mM, $c_{\text{IQCA}} = 0.25$ mM, pH=7.4, $\lambda_{\text{exc}} = 326$ nm)



285 nm), another organic ligand as the antenna for sensitization of Ln(III) ion luminescence was screened. Adding one benzene ring to the picolinic acid structural motif to shift excitation wavelength maximum to the red, the quino-line/isoquinoline-carboxylic acid derivatives can be taken into account. Various ligands having this structural motif were tested and the isoquinoline-3-carboxylic acid (IQCA) was found as the best one. The formed [Eu(DO3A)(IQCA)]⁻ ternary complex shows slightly higher luminescence enhancement compared to the picolinate complex simultaneously with the red shift of the excitation wavelength maximum to 326 nm. The luminescence intensity of the Eu(DO3A)(IQCA)]⁻ ternary complex increased ~230-times compared to the binary [Eu(H₂O)₂(DO3A)] complex. It is also higher than that of the Eu(DO3A)(picolinate)]⁻ sensor probably as consequence of formation of more thermodynamically stable complex where Eu(III) ion is efficiently shielded from quenching by water molecules. Unlike to the picolinic acid containing system (see Fig. 1), a higher concentration of the free ligand, ICQA, does not cause the self-quenching of luminescence of its ternary complex (Fig. 9a). Thus, the red shift of excitation maximum about 40 nm to the VIS range together with suppression of self-quenching yields a sensor with better optical properties.

Because the response function of IQCA sensor is in many aspects similar to that of the picolinate one, therefore, the same optimized experimental conditions (e.g. $c_{EuL} = 0.1$ mM, pH=7.4) were employed. The analytical parameters of the method such the sensitivity and detection limit (114 ± 2 M⁻¹; $c_{ICQA} = 0.2$ mM) were determined from calibration curve (see Fig. 9b) and were found to be very similar for both Ln(III)-H₃DO3A-PA sensors. To simplify the whole analytical procedure for the blank correction for dissolved bicarbonate present in distilled water (0.72 mM, i.e. 4.32 mg L⁻¹—see previous paragraphs), all solutions of the reagents were prepared in distilled water free of dissolved carbon dioxide. This procedure is highly recommended since the content of bicarbonate in blank can be changed with time (see Table 3). It was verified by analysis of the blank sample of such distilled water where the concentration of bicarbonate in the CO₂-free distilled water sample was found to be below detection limit of the method. Then, the procedure using both PA and IQCA sensors was verified using a set of international mineral water samples (France, Italy and Czech Republic) displaying low, medium and high bicarbonate content and overall mineralization (Table 3). Both PA and IQCA sensors have a good sensitivity which has not changed with the overall composition of the samples. Both the results of analysis are comparable to the

Table 3 The results of bicarbonate analysis of mineral waters

Sample	(HCO ₃) ⁻ Content (mg dm ⁻³)		Sensor sensitivity (dm ³ mg ⁻¹)		
	Declared ^{a,b,c}	Found with Eu(III) sensor		PA	IQCA
		PA	IQCA		
Distilled water		0.65(2)	1.13(5)	0.66(3)	0.67(3)
Evian (FR) ^{d1}	360 ^a ; 360 ^b ; 357 ^c	218(7)	394(21)	0.63(3)	0.69(3)
Vittel (FR) ^{d2}	248 ^a ; 399 ^b ; 258 ^c	190(5)	253(9)	0.77(2)	0.70(2)
Aqua Panna (IT) ^{d3}	103 ^a ; 106 ^b ; 100 ^c	206(9)	118(4)	0.69(3)	0.65(2)
San Pellegrino (IT) ^{d4}	239 ^a ; 239 ^b ; 136 ^c	290(9)	228(7)	0.65(3)	0.71(3)
“Bilinská kyselka” (CZ) ^{d5}	4545 ^a ; 4482 ^b ; 4471 ^c /4491 ^c	3808(275)	4143(104)	0.84(5)	0.71(2)
“Vincentka” (CZ) ^{d6}	4853 ^a ; 4853 ^b ; 3989 ^c	3916(268)	3945(207)	0.83(5)	0.76(3)

The SD values are given in the parantheses

^a Bottle label

^b Official websites (Evian—http://www.evian.com/en_INT; Vittel—<http://www.vittel.com/>, San Pellegrino, Aqua Panna—<http://www.sanpellegrino.it/>, Czech mineral waters: <http://bilinskakyselka.cz/>, <http://www.vincentka.cz/cs>)

^c “Mineral Waters of the World” (<http://www.mineralwaters.org>)

^d Chemical composition of analyzed mineral waters (in mg dm⁻³):

1) Na⁺ 5.0; K⁺ 1.0; Mg²⁺ 24; Ca²⁺ 78; Cl⁻ 4.5; NO₃⁻ 3.8; SO₄²⁻ 10; SiO₂ 13.5 (total mineralization 357)

2) Na⁺ 7.3; K⁺ 4.9; Mg²⁺ 19.9; Ca²⁺ 91; Cl⁻ 3.7; SO₄²⁻ 105; F⁻ 0.6 (total mineralization 403)

3) Na⁺ 6.5; K⁺ 0.9; Mg²⁺ 6.9; Ca²⁺ 30.2; Cl⁻ 7.1; SO₄²⁻ 21.4; NO₃⁻ 5.7; SiO₂ 8.2 (total mineralization 137)

4) Na⁺ 43.6; K⁺ 2.7; Mg²⁺ 55.9; Ca²⁺ 208; Cl⁻ 74.3; SO₄²⁻ 549.2; NO₃⁻ 0.45; F⁻ 0.52; Br⁻ 0.38; SiO₂ 9 (total mineralization 1109)

5) Li⁺ 3.72; Na⁺ 1792; K⁺ 89.33; Mg²⁺ 41.90; Ca²⁺ 133.70; F⁻ 5.10; Cl⁻ 231; SO₄²⁻ 542; (total mineralization 7389.87)

6) Li⁺ 11.10; Na⁺ 2447; K⁺ 134.0; NH₄⁺ 10.70; Mg²⁺ 15.60; Ca²⁺ 258.0; Sr²⁺ 4.35; Ba²⁺ 6.99; Fe²⁺ 4.15; Mn²⁺ 0.579; Al³⁺ 0.214; Zn²⁺ 0.0742; F⁻ 3.08; Cl⁻ 1761; Br⁻ 6.85; I⁻ 6.36; SO₄²⁻ 1.20; HCO₃⁻ 4853; NO₃⁻ 0.840; HBO₂ 311.0; H₂SiO₃ 17.60; (total mineralization 9854)

mineral content listed on the bottle label as well as at the manufacturer's official website; however, the official concentrations differs from each other in many cases as well as from the "semi-official" data from "Mineral Waters of the World" (see <http://www.mineralwaters.org>—website devoted to the mineral waters contents from several independent water analyses. In addition comparing the bicarbonate content and sensor sensitivity, it seems that the more reliable results are obtained with the more robust IQCA sensor than those with the PA one. It was also demonstrated that the results can differ since the major analytical technique for determination of the bicarbonate content in mineral water springs is acidimetric titration [42] which can be loaded by error in presence of other species having acid-base properties. Also bicarbonate content can fluctuate with time as it has been proved by CITP analysis of mineral water for Ca^{2+} , Mg^{2+} , K^+ , Na^+ , Cl^- , SO_4^{2-} and HCO_3^- ions [43, 44]. In addition, some results-outliers of mineral water analysis were described [44] which too contribute to the overall uncertainty regarding the bicarbonate and mineral levels in beverages and consumer products. This also illustrates that a new simple and robust method for determination of bicarbonate in water are still required which is subject of this study.

Conclusion

The bound water molecules in the $[\text{Eu}(\text{H}_2\text{O})_2(\text{DO3A})]$ complex undergo substitution with various anions to form stable ternary adducts having longer luminescence life times than the original diaqua complex due to the absence of coordinated water molecules in the ternary complex. The stability constants values of the ternary $\text{Eu}(\text{III})\text{-H}_3\text{DO3A}$ -ligand complexes with bidentate ligands follow the order $\text{CO}_3^{2-} > \text{oxalate}^{2-} > \text{picolinate}^- > \text{phthalate}^{2-} \approx \text{citrate}^{3-}$. This order reflects differences in the steric requirements and/or basicity of the bidentate ligands. The ternary complexes $[\text{Ln}(\text{DO3A})(\text{L})]^-$ ($\text{Ln} = \text{Eu}, \text{Tb}$; $\text{L} = \text{picolinate}, \text{isoquinoline-3-carboxylate}$) can be used for a sensitive determination of carbonate/bicarbonate and oxalate anions in the millimolar concentration range. The optimal experimental conditions are: $\text{pH} > 7$, $c_{\text{Ln}} = 0.1 \text{ mM}$ and $c_{\text{PA}} = 5 \text{ mM}/c_{\text{IQCA}} = 0.25 \text{ mM}$. The presence of other anions (e.g. citrate, phthalate) does not interfere with the determination. The proposed analytical procedure can be used for a fast, selective and sensitive determination of a carbonate concentration in water samples under aerobic conditions. It can be also automatized for routine analysis as luminescence bicarbonate assay using a microplate reader [26]. The procedure can be also employed for analysis of water samples concerning complex matrix of other ionic species where ion chromatography as the dominating technique for ion analysis does have practical problems [45].

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