

A MODEL STUDY OF PH EFFECT ON ENAMINONE COMPLEXATION ACTIVITY TOWARDS SOME METALS

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Abstract

Enaminones were tested as potential complexation agents towards a group of metal ions (Al, Na, Ba, Ca, Mg, Fe, Ti, Cr, Mn, V, Cu, Zn, Pb, La, Ce, Eu, Gd, Er) and the effect of sample solution pH on extraction degrees was studied. Residual concentrations of metals in the water phase were determined by Inductively Coupled Plasma Mass Spectrometry and Inductively Coupled Plasma Optical Emission spectrometry after classical liquid-liquid extraction. Ligand selectivity towards all analytes was studied. Enaminones showed promising results as lanthanide-selective reagents.

Key words: Enaminones, liquid-liquid extraction, lanthanides, rare Earth elements, ICP-MS

1. INTRODUCTION

Rare Earths Elements (REEs) have been widely used during the last few decades. Due to their valuable properties they have found application in various areas namely ceramics, metal alloys, batteries, high power and high temperature magnets, lasers, liquid crystal displays, magnetic resonance imaging contrast agents, solar panels, etc. [1].

Intensive use of REEs increases emissions into the environment, resulting in raising concentrations significantly over their natural distribution. In general, there are limited studies on the environmental and human health impacts of REEs [2,3,4].

Determination of lanthanides in environmental samples is a difficult task because of analytes low concentrations and diversity of sample matrices. Very sensitive and selective techniques should be used for quantitative analysis of these elements. Neutron activation analysis was successfully applied for trace levels determination in biological samples [5] and brain tissues [6]. The high cost of the instrumentation and difficulties in calibration limit its use in screening assays of ecological entities.

ICP-MS has been established as one of the most powerful instrumental techniques for multielemental trace analysis, but it also has some limitations. Determination of lanthanides in real samples with variable matrix (as natural waters, plants and soils) suffers from spectral interferences - isobaric and polyatomic. An effective way of overcoming these limitations is the preliminary separation of analytes from interferents [7, 8, 9].

Various separation techniques are reported in scientific literature. Classical liquid-liquid extraction is a fast, effective and easy to perform technique for separation of target analytes. Often the preliminary separation of analytes in the organic phase is followed by back extraction into water media, because of instability of ICP when organic solvents are nebulized [9, 10].

Recently several preconcentration techniques became popular as greener alternatives to solvent extraction. Dispersive liquid-liquid micro extraction (DLLME) combines modern trends of miniaturization and automation with well-studied fundamentals of classical solvent extraction. The DLLME methods for simultaneous preconcentration were successfully combined with ICP-MS for determination of 14 lanthanides at parts per trillion levels in groundwater [11], and with ICP-OES for determination of Sm, Eu, Gd and Dy [12].

Cloud point extraction replaces toxic organic solvents used for extraction, with more ecologically benign surfactants. A method for CPE of lanthanide ions with Triton X-100 has been developed by Mustafina et. al. [13].

Ion exchange with chelating resins followed by ICP-MS has also been used for matrix separation and preconcentration of REEs from seawater [7, 8].

Different types of compounds have been applied for coordination of lanthanides: polymers [14], organophosphorus compounds [9,10], calixarenes [13], 2,6-pyridinedicarboxylic acid (2,6-PDCA) in the presence of Aliquat 336 (tricaprylmethylammonium chloride) [11], PAN 1-(2-pyridylazo)-2-naphthol [12], diglycolamides [15] and different chelating ion exchange resins [8].

Although various types of reagents have been developed, design of new compounds, particularly those with selectivity for specific metal ion separation, is still highly demanding. In this particular study the efficient separation of REEs from essential macro-components of real environmental samples as alkali and alkaline earth elements and some concomitant metals is strongly desired in order to avoid spectral interferences during ICP-MS measurement of target analyte group at part per billion levels.

The complexation activity of two enaminone [2-(2-Carbamoyl-1-methyl-vinylamino)-ethyl]-carbamic acid tert-butyl ester (Enaminone 1 – Figure 1) and [2-(1-Methyl-2-phenylcarbamoyl-vinylamino)-ethyl]-carbamic acid tert-butyl ester (Enaminone 2 – Figure 2) is tested in this study. Enaminones were selected as promising ligands metal ions because of the nitrogen, oxygen and conjugated system that their structures contain. To best of our knowledge compounds of this type were not used for matrix separation and concentration of metals in water medium.

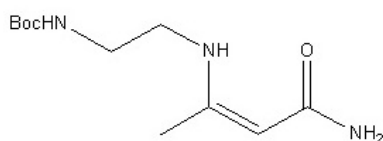


Figure 1 Enaminone 1

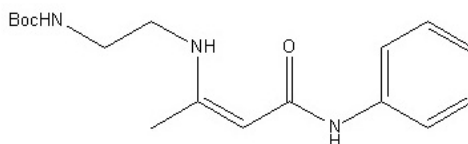


Figure 2 Enaminone 2

Boc – tert-butoxycarbonyl

2. Experimental

a. Reagents and standard solutions

Monoelemental solutions:

Ce, Er, Eu 1000 mg.l⁻¹, CPA-spectrTM

Gd₂O₃, 99,9%, Sigma-Aldrich

La(NO₃)₃, 99%, Sigma-Aldrich

K, Na, S, Mg, Ba 1 mg.l⁻¹, Sigma-Aldrich

Ca 1 mg.l⁻¹, Merck, Darmstadt, Germany

Multielemental solution, 100 mg.l⁻¹ Spectracor Ref. № M001100

NH₄OH, p.a., Merck, Darmstadt, Germany

HNO₃, p.a., Merck, Darmstadt, Germany

CHCl₃, p.a., Merck, Darmstadt, Germany

Double distilled water was used for the preparation of all solutions.

b. Instrumentation

2.2.1 ICP-MS Agilent 7700 (Tokyo, Japan)

Plasma conditions	
RF Power	1.5 kW
Ar Plasma gas -	15 l.min ⁻¹
Nebulizer	Micromist (Glass Expansion)
Auxiliary gas flow rate	0.9 l.min ⁻¹
Spray chamber	Scott double pass
Interface cones	Ni
Collision gas	He - 3,5 ml.min ⁻¹
Pump speed	0,1 rpm
Mass spectrometer	
Resolution	0,65 amu
Measurement mode	Peak hoping
Points per peak	3
Acquisition time	0,1 s

Table 1 ICP-MS working conditions

2.2.2 ICP- OES iCap6000 Thermo Scientific

	UV	VIS
Exposure time	15 s	5 s
RF power	1,150 kW	1,150 kW
Nebulizer gas	0,5 l/min	0,5 l/min
Auxiliary gas	0,5 l/min	0,5 l/min
Pump speed	0,5 rpm	0,5 rpm
Measurement mode	radial/axial	

Table 2 ICP-OES working conditions

2.2.3 pH-meter - pH Checker, Hanna Instruments Inc

2.2.4 Low speed centrifuge KA-1000, Kubota Corporation

c. *Ligands synthesis*

Enaminones were synthesized according to a previously published procedure [16].

d. *Extraction procedure*

Working solutions were prepared by diluting standards with double distilled water. Gd₂O₃ and La(NO₃)₃ solutions were prepared by dissolving the salts in diluted nitric acid. Extraction procedures were carried out in 14 ml conical test tubes as it follows: 2 ml of 0,03 M chloroformic solution of the ligand was mixed with 10 ml 100 µg.l⁻¹ multielemental solution (Metals:Ligand~1:100 molar ratio). pH of the water phase was adjusted to the desirable value by addition of 1 M NH₄OH (pH=5-9±0.2).

For evaluation of interference effect from concomitant elements 1 mg.l⁻¹ of K, Na, Sr, Mg, Ba and Ca were spiked to a set of the as prepared samples.

Solutions were shaken for 2 minutes and then centrifuged for 5 minutes at 3000 rpm. Back extraction was done by addition of 10 ml 1M HNO₃ to the carefully separated organic phase containing the obtained complexes. Residual metal concentrations in the water phase and concentrations after back extraction were determined by inductively coupled plasma mass spectrometry. K, Na, Sr, Mg, Ba and Ca were measured by inductively coupled plasma optical emission spectrometer.

3. RESULTS AND DISCUSSION

Evaluating the extraction degree of metals (by measuring the residual concentration of tested elements in water phase) was considered enough for introductory estimation of complexation activity of studied ligands, as it is easy and convenient and does not include steps of separation and re-extraction of analytes.

Extraction degrees of metals are calculated as difference between initial (C_0) and residual concentration (C) of metals in the water phase, divided into the initial concentration, in percentage.

$$E, \% = \frac{(C_0 - C) \times 100}{C_0} \quad (1)$$

For estimation of spectral interferences arising from plasma components, reagents needed for the extraction procedure and CHCl₃ (solubility in water 0,8 g/100 ml, 20°C) analyte concentrations were measured in standard “No Gas” mode and using collision cell “He gas” mode. Although He gas was applied some of the analytes suffer from severe spectral interferences and could not be measured under these conditions. The least interfered isotopes were selected for evaluation of extraction degrees (²⁷Al, ⁴⁷Ti, ⁵¹V, ⁵³Cr, ⁵⁸Fe, ⁶⁸Zn, ¹¹⁴Cd, ¹³⁹La, ¹⁴⁰Ce, ¹⁵³Eu, ¹⁵⁸Gd, ¹⁶⁸Er, ²⁰⁸Pb).

Nonspectral matrix effect was not observed and thus not corrected. Sensitivity drift was corrected by periodical measurement of check standards and recalculation of analyte concentration.

Solvent extraction was chosen for initial experiments because of its simplicity, accessibility, ease of use and low price. As one of the most significant factors in complex-formation reactions affecting both metal ions and ligands, pH of the water phase was varied from 5 to 9. Experiments in strongly acidic media (pH<5) were not done to avoid hydrolysis of the ligands. pH=9 was chosen as the end point of current study, as most of the analytes precipitate in basic solutions. Obtained results are shown on Figures 3-7.

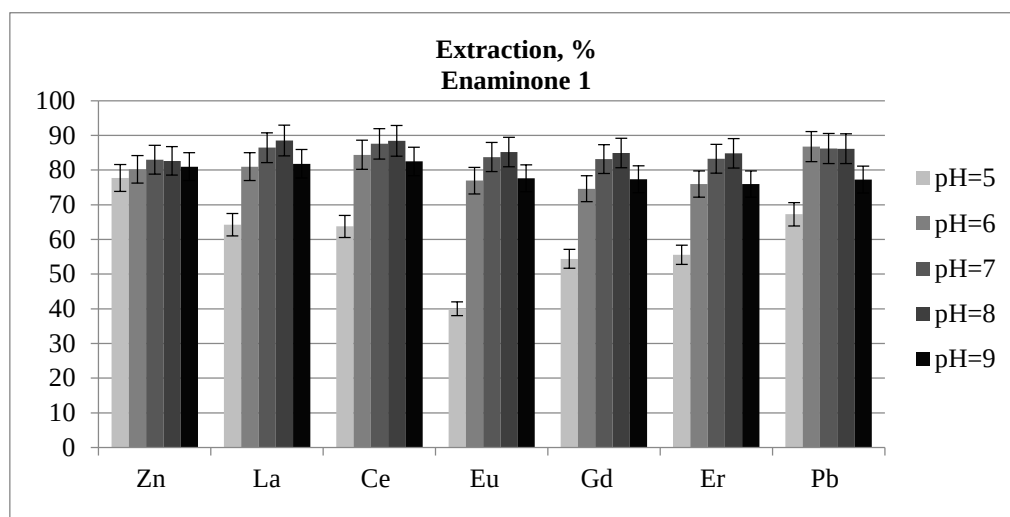


Figure 3 Extraction degrees, % Zn, Pb and lanthanides with Enaminone 1

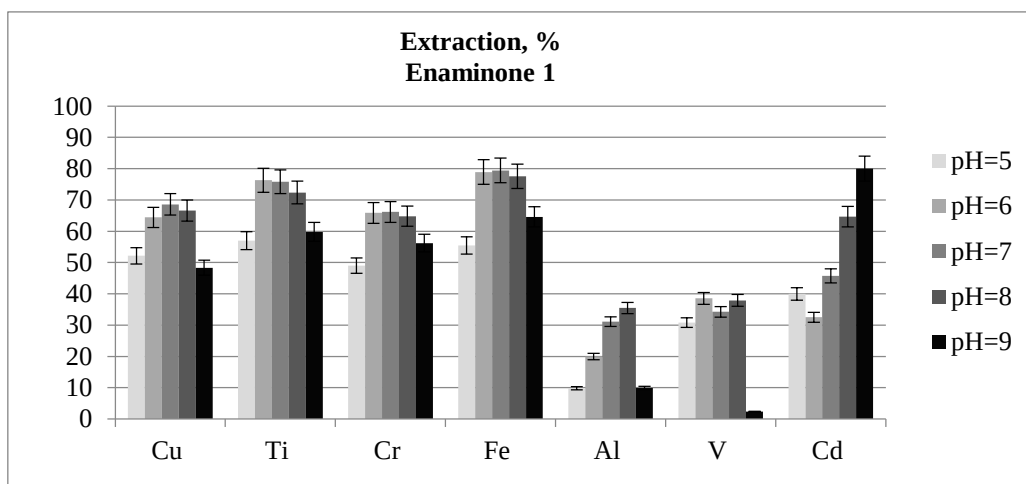


Figure 4 Extraction degrees, % Cu, Ti, Cr, Fe, Al, V with Enaminone 1

Extraction degrees of studied REE, Pb and Zn with Enaminone 1 vary between 75 and 88% in pH range 6-8 (Fig. 3). Efficiency of complex formation decreases in both ends of studied pH interval. The observed decrease of extraction degrees for REE at pH=5 is probably due to competitive protonation of coordination sites of the ligand. The ~10% reduction of extraction degree at pH = 9 is probably due to binding of metal ions in stable hydroxides. The only exception was observed for Zn, where the extraction degrees are statistically identical for the entire investigated pH range.

The optimum part of pH range for effective extraction of REE, Pb and Zn with Enaminone 1 is at neutral or weak basic range (pH ~7-8).

Figure 4 presents results for some partially co-extracted elements with Enaminone 1. The extraction degrees for other tested elements vary from ~78 % (Ti and Fe) to ~66% (Cu and Cr). Negligible extraction was obtained for Al and V (<38%). Extraction effectiveness for Cd strongly depends on pH with a clear trend of increasing in basic media.

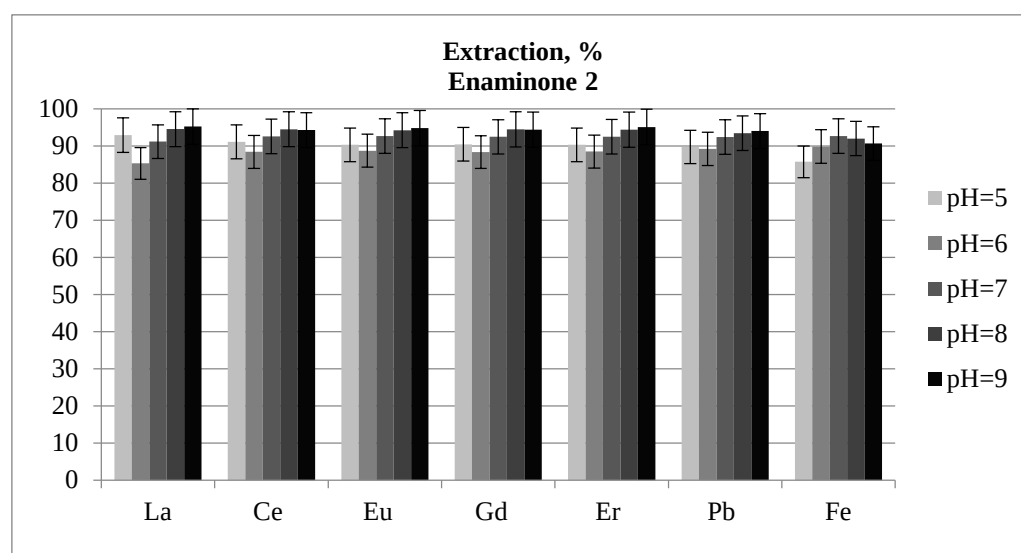


Figure 5 Extraction degrees, % Pb, Fe and lanthanides with Enaminone 2

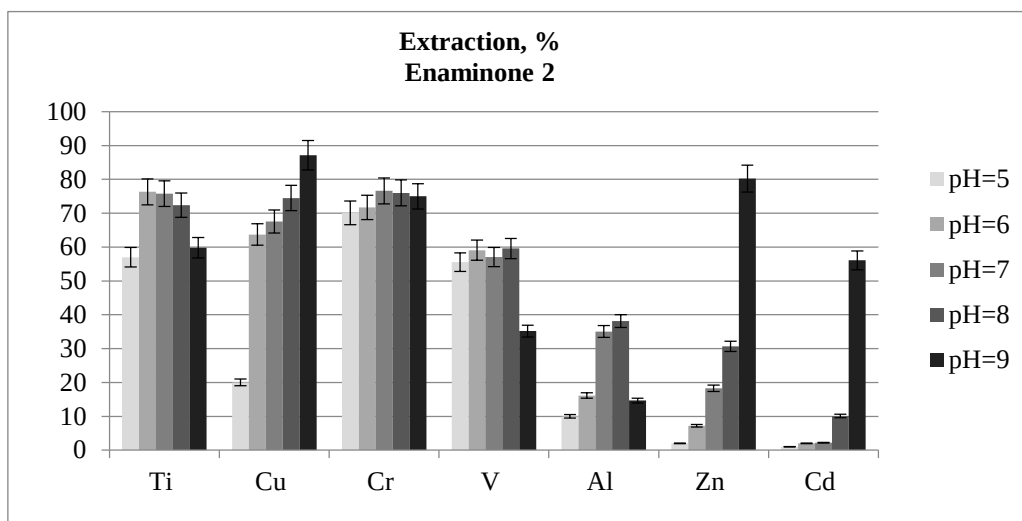


Figure 6 Extraction degrees, % Ti, Cu, Cr, V, Al, Zn, Cd with Enaminone 2

Enaminone 2 shows better complexation activity towards all metals which might be due to its more hydrophobic structure that could allow better separation of complexes from the water phase. According to the obtained results for Enaminone 2 the tested elements could be divided into three groups:

- quantitatively extracted elements ($E\% > 90$) for which reaction does not strongly depend on pH: La, Ce, Eu, Gd, Er, Pb and Fe (Fig. 5);
- partially extracted elements for which reaction does not depend on pH: Ti ($E \sim 80\%$), Cr ($E \sim 70\%$), V ($E \sim 60\%$); (Fig. 6);
- pH-dependable extraction with a clear trend of increasing in the basic media - Cu, Zn, Cd (up to 85, 80 and 58% respectively at pH=9). The extraction degree for Al is below 40% at optimal pH value of 8.

The different behavior of the metals, depending on the type of enaminone and pH, could be used for preferential extraction of target analyte groups. The most effective extraction was obtained for lanthanides, Pb and Fe with Enaminone 2. Performing this reaction in slightly acidic solutions the co-extraction of concomitant Cu, Zn, Cd and Al could be kept at comparatively low levels improving the selectivity.

One of the main reasons for new selective ligands research is the need to find novel reliable extractants which could be applied to real sample analysis especially when analytes are in very low (sub ppb) concentrations and matrix elements are presented in much higher levels. The typical high salt content of natural waters (mostly alkali and alkaline earths salts) may cause formation of radicals interfering REEs. Some of the interfering ions are shown on Table 3.

It should be noted that in the table is represented only one isobaric (Ba and Ce at 136 amu), but the problem with a plurality of different types of polyatomic species can significantly complicate the analysis of real samples when concomitant interfering components present in the matrix.

Hence, if lanthanides should be directly analyzed in natural waters containing alkali and alkaline earth elements in much higher concentration, severe spectral overlaps could be expected.

Isotope	Interfering ion (probability of formation based on natural abundance of isotopes)
^{138}La	$^{69}\text{Zn}^{69}\text{Zn}$ (0,24%), $^{137}\text{Ba}^1\text{H}$ (11,23%)
^{139}La	$^{138}\text{Ba}^1\text{H}$ (71,7%)
^{136}Ce	^{136}Ba (7,85%), $^{68}\text{Zn}^{68}\text{Zn}$ (4%),

^{151}Eu	$^{111}\text{Cd}^{40}\text{Ar}$ (12,756%), $^{116}\text{Cd}^{35}\text{Cl}$ (12,64%), $^{135}\text{Ba}^{16}\text{O}$ (6,575%)
^{153}Eu	$^{113}\text{Cd}^{40}\text{Ar}$ (12,171%), $^{116}\text{Cd}^{37}\text{Cl}$ (1,82%), $^{137}\text{Ba}^{16}\text{O}$ (11,219%)
^{154}Gd	$^{114}\text{Cd}^{40}\text{Ar}$ (28,62%), $^{136}\text{Ba}^{16}\text{O}$ (71,55%)
^{168}Er	$^{84}\text{Sr}^{84}\text{Sr}$ (0,003%)
^{170}Er	$^{85}\text{Sr}^{85}\text{Sr}$ (0,11%), $^{135}\text{Ba}^{35}\text{Cl}$ (4,993%)

Table 3. Polyatomic and isobaric interferences, arisen from matrix components and plasma gases, overlapping REE isotopes

For this reason the possibility to separate REEs from typical for natural matrix concomitant elements as: Sr, K, Mg, Na, Ca, Ba by extraction with enaminones is studied. The selectivity of complex formation towards alkali and alkali earth elements is studied in two stages. In the first step, the possibility to involve interfering elements in a reaction with enaminones was estimated by measuring residual concentration of alkali and alkali earth elements in the water phase after extraction performed at optimum conditions for REE. The measurement was done by ICP-OES and results are presented as percentage of remaining interferents after extraction.

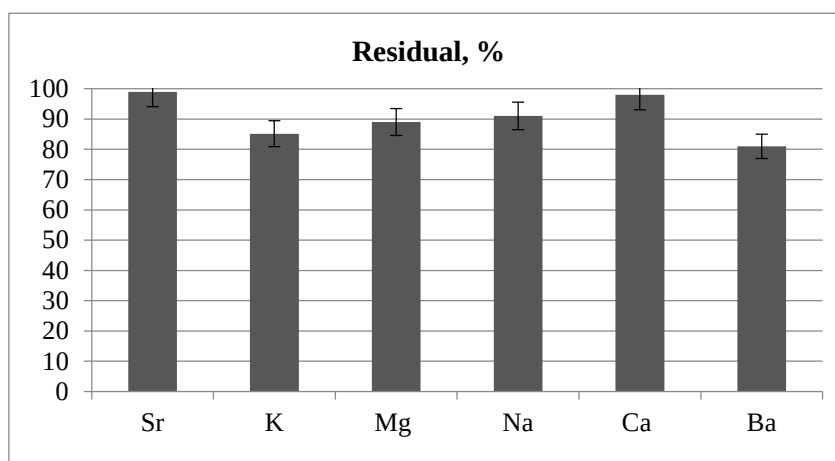


Figure 7 Residuals, % of Sr, K, Mg, Na, Ca, Ba in water phase after extraction.

From the results presented on Figure 7 is clear that more than 80% of studied concomitant elements remain in the water phase, hence the enaminones do not bind to alkali and alkaline Earth metals under the optimized experimental conditions for extraction of trace metals. Therefore, the studied compounds are promising for effective matrix separation in real water samples prior to lanthanides analysis.

The effect of typical macrocomponents (alkali and alkaline Earth elements) in natural water samples on extraction of lanthanides was also studied and evaluated by tracing the change of analytes recovery after back extraction with HNO_3 in both presence and absence of interfering ions. It should be noted that separation of the phases must be done very carefully as some of the complexes turned out to be insoluble in both water and chloroform and formed very fine third solid layer between the solvents. The recovery of analytes is calculated by dividing the measured concentration after back extraction C_{re} into the initial concentration of spiked metals C_0 , in percentage:

$$R, \% = \frac{C_{re} \times 100}{C_0} \quad (2)$$

Recoveries of analytes in water samples and water samples spiked with 1 mg.l^{-1} Ca, Sr, Ba, Mg, Na and K are compared, when extraction of REEs with Enaminone 2 is performed in acidic (pH=5, Fig.8) and basic (pH=8, Fig. 9) media.

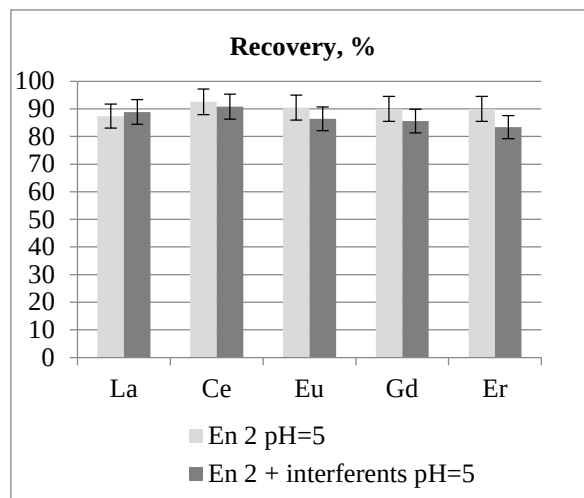


Figure 8 Recovery of lanthanides in water samples and water samples spiked with 1 mg.l^{-1} Ca, Sr, Ba, Mg, Na and K

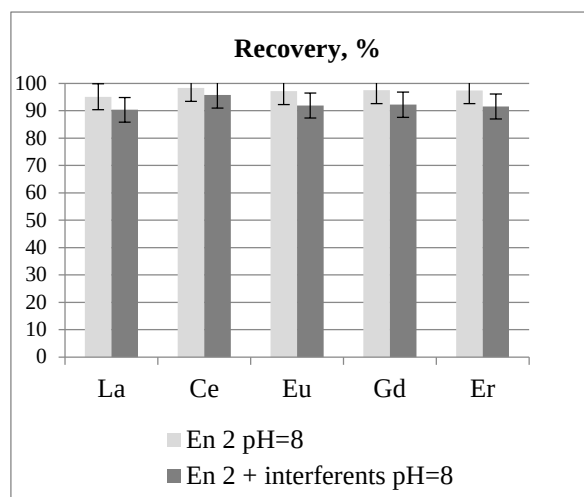


Figure 9 Recovery of lanthanides in water samples and water samples spiked with 1 mg.l^{-1} Ca, Sr, Ba, Mg, Na and K

Quantitative recoveries of lanthanides in the presence of interfering ions show good selectivity for analytes with respect to alkali and alkaline earths elements. If the real sample contains Cadmium, which could be partially co-extracted at pH=8, an effective way for successful elimination of interference effect due to this element is to increase selectivity by performing extraction in slightly acidic media, where the degree of co-extraction is negligible.

Detection limits (3sd) and limits of quantification (10sd) for REEs, shown on Table 4, are calculated after the extraction procedure at optimal conditions.

	^{139}La	^{140}Ce	^{151}Eu	^{156}Gd	^{167}Er
DL, $\mu\text{g.l}^{-1}$	0,006	0,013	0,007	0,038	0,004
LQ, $\mu\text{g.l}^{-1}$	0,012	0,017	0,011	0,065	0,009

Table 4 Detection limits and limits of quantification for REEs after extraction (No Gas mode)

Achieved detection and quantification limits (ppt) for analytes in samples after extraction procedure are lower than the expected levels of REEs concentration in natural waters, hence the further development of the studied procedure for real sample analysis is promising.

CONCLUSIONS

From the obtained results can be concluded that the studied compounds have strong affinity to lanthanides and some other elements, depending on the enaminone used. The pH of the sample solution does not significantly affect on the complex formation reaction of rare earth elements, but the efficiency of the extraction of some undesirable metal ions can be noticeably reduced by the change of pH and the type of selected ligand. Enaminones show high potential to be successfully used as new ligands for matrix separation and concentration of lanthanides from aqueous media as macro components of water samples, as alkali and alkaline earth metals, do not affect target extraction.

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