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Cloud point extraction of lanthanides with 3-ethylamino-but-2-enoic acid phenylamide from water samples prior to ICP-MS determination

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A compound representative of the enaminones class is studied as a new ligand for Cloud Point Extraction (CPE) of lanthanides (La, Ce, Eu, Gd, Er) from aqueous medium. Extraction parameters such as water phase pH, heating temperature, incubation time, type and quantity of surfactant are optimized. Analyte concentrations are measured by ICP-MS after appropriate dilution of the surfactant-rich phase. The extraction system based on the new ligand showed high efficiency for separation of lanthanides from concomitant alkali and alkaline earth elements, which significantly reduces the risk of spectral interferences in real samples. Selectivity of the tested enaminone is compared to the classical ligand 8-hydroxyquinoline. The instrumental drift in sensitivity is corrected by internal standardization with Re. The optimized procedure is applied on water certified reference material and real water samples. Obtained limits of detection are in the interval 0.2-1.3 ng L^{-1} with 10-fold preconcentration.

Keywords: *Lanthanides, Cloud Point Extraction, Enaminones, ICP-MS, Water Analysis.*

INTRODUCTION

Cloud point extraction (CPE) is a green alternative to classical extraction techniques that doesn't require use of toxic, volatile and flammable solvents [1]. Due to its advantages, CPE has been extensively used in the last decades for separation and preconcentration of organic [2-4] and inorganic [5-7] substances. Extraction of metal ions is principally performed by preliminary formation of water insoluble complexes with variety of ligands: pyridylazo and thiazolylazo derivatives, such as 1-(2-pyridylazo)-2-naphthol (PAN), 1-(2-thiazolyazo)-2-naphthol (TAN), 4-(2-pyridyl-azo) resorcinol (PAR), 2-(5-bromo- 2-pyridylazo)-5-(diethylamino) phenol (5-Br-PADAP), ammonium pyrrolidinedithiocarbamate (APDC), diethyldithiocarbamate (DDTC), 2-amino-cyclopentene-1-dithiocarboxylic acid (ACDA), O,O-diethyldithiophosphate (DDTP), 8-hydroxyquinoline (oxine, 8-HQ) and dithizone [8]. Still few authors report procedures for CPE of lanthanide ions (Ln) with ligands as Alizarin Red S and cetyltrimethylammoniumbromide (CTAB) [9], water-soluble calixarenes [10], hydrophobic calixarene platforms [11], 8-hydroxyquinoline[12, 13] and 2-(5-bromo-2-pyridylazo)- 5-diethylaminophenol [14].

ICP-MS is considered to be one of the most appropriate techniques for lanthanide analysis in diversity of real samples [15-17]. Nevertheless, the direct determination of these elements is hindered by spectral interferences caused by barium [18, 19]. Most of the authors recommend separation procedure before the measurement [20].

In this study is presented the potential of enaminones (En) as ligands for CPE of lanthanides from water samples.

EXPERIMENTAL

Instrumentation

All measurements are performed with ICP-MS Agilent 7700. The measurements were done using standard plasma operating conditions; Micromist (Glass Expansion) nebulizer, using normal resolution (0.65 amu); 5 replicates per sample; 1 point per mass peak and 0.1s acquisition time. Two isotopes per analyte were monitored ^{140,142}Ce, ^{151,153}Eu, ^{156,157}Gd, ^{166,168}Er with exception of lanthanum where only one isotope is free from isobaric interference ^{139}La.

Reagents and standard solutions

All reagents and solvents were analytical grade and used without further purification. Monoelemental solutions of Ce, Er, Eu (1000, mg L^{-1}) were purchased from CPA-spectr^{TM}. Solutions for La and Gd with concentration 1000 mg L^{-1} were prepared by dissolving of Gd_2O_3 (99,9%, Sigma-Aldrich) and $La(NO_3)_3{\cdot}6H_2O$ (99,99%, trace metals basis, Sigma-Aldrich) in 1 mol L^{-1} HNO_3 (p.a.,Merck) on heating plate and then diluting with double distilled water. Stock

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solution of Re (1000 mg L^{-1}) was obtained from Merck (Darmstadt, Germany). Selectivity test was performed using Multi elemental solution, 100 mg L^{-1} CPA Chem Ref. № B56A.K1.5N.L1. A buffer solution with pH=8.3 was prepared from NH_4OH and NH_4NO_3 (Merck). Certified reference material for surface water SPS Quality Level 1 (Spectrapure standards, Oslo, Norway) was used for method validation. Triton X-100 (TX-100, Merck) and Triton X-114 (TX-114, Fluka AG) were tested as surfactants for CPE. 8-Hydroxyquinoline (Sigma-Aldrich) was used for selectivity comparison.

3-ethylamino-but-2-enoic acid phenylamide (En) was synthesized according to a procedure described by Venkov and Angelov in [21].

Cloud point extraction of lanthanides with tested enaminone

Calibration standards and model solutions were prepared in plastic test tubes as it follows: 40 mL of tested water solution containing target lanthanide ions 1 µg L^{-1} (and concomitant elements 10 µg L^{-1}) was buffered at pH=8.3 by the addition of 5 mL NH_4OH/NH_4NO_3 buffer solution. Then 0.2 mL (0.06 mol L^{-1}) solution of the ligand in ethanol was added and the sample was shaken for 2 minutes. Finally, 5 mL 10 % TX-100 were added and test tubes were placed in water bath for 30 minutes at 70°C. After incubation, samples were cooled in freezer. Then the water phase was removed with pipette and surfactant rich phase (SRP) was diluted with 1 mol L^{-1} HNO_3 with internal standard (IS) Re to final volume of 4 mL. Procedural blank was also prepared.

Real samples and Reference material

SPS Water Level 1: Acidified surface water samples were neutralized to pH~5 and then prepared according to the procedure for model solutions.

Cloud point extraction of lanthanides with 8-hydroxyquinoline

The method for CPE with 8-HQ described elsewhere [12] with slight modification - i.e. the SRP was directly diluted with 0.01 mol L^{-1} HNO_3 (with IS Re) after CPE.

RESULTS AND DISCUSSION

Optimization of extraction parameters for CPE with enaminone

The optimization of extraction parameters was started with pH of the initial aqueous solution because it affects both ligand's and analytes' behavior. In our previous studies on liquid-liquid extraction, we found that the highest efficiency of the reaction between lanthanides and enaminones was achieved in basic medium [22, 23]. The investigated pH range here (from 6 to 9) confirmed that in acidic and strong basic medium the complex formation is suppressed. Expectedly, the highest signals were obtained for pH=8 and for this reason, NH_4NO_3/NH_4OH with pH~8.3 was used for further experiments.

CPE was tested at the optimum pH value without the addition of ligand because the lanthanides are partially hydrolyzed in basic medium; their hydrophobic hydroxides could be extracted in SRP. Furthermore some authors have reported high yields for lanthanides obtained by CPE in basic (pH>9) [24] and even in acidic media [13] without addition of ligand. The results presented in Figure 1 indicate that ligandless extraction is possible but with low efficiency. The presence of tested enaminone results in a twofold increase in the signals for all elements and ensures higher recoveries.

In addition, it was discovered that the order of mixing the reactants during the sample preparation also influences the signals. Up to 30% lower signals are measured when the surfactant is added before the ligand. This is probably due to the higher solubility of the ligand in a micellar phase formed by surfactant, which decreases its concentration in the aqueous phase before completing the reaction with target ions. Therefore, it is recommended to add firstly the ligand to the sample solution and after vigorous stirring, to introduce the surfactant.

The concentration TX-100 was varied in the interval 0.5-5%, in order to define the minimal amount of surfactant needed for extraction of lanthanides, keeping all other parameters constant. It was established that 1% TX-100 is sufficient for quantitative extraction of the analytes.

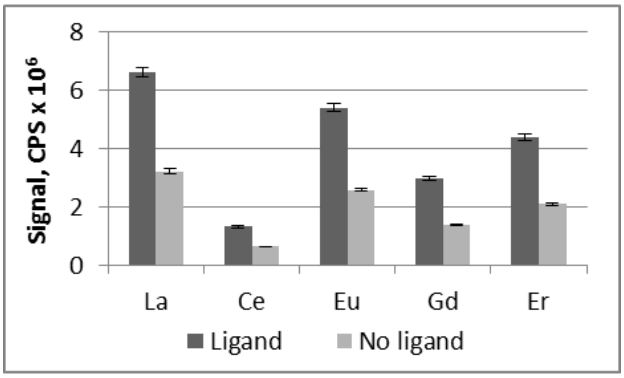

Figure 1. Signals for lanthanides after dilution of SRP with 1 mol L^{-1} HNO_3 with and without ligand. Constant conditions: pH=8.3; C_{Ln}=1µg L^{-1}; 12 µmol Enaminone; 1% TX-100; incubation time of 1 hour, t=70°C; dissolution of SRP - 1 mol $L^{-1}$$HNO_3$.

The incubation time affects both the duration of CPE and its effectiveness, so it is tested on four levels (15, 30, 45 and 75 min.). The signals for all test elements are increased by ~ 25% at an incubation time of 30 minutes in comparison to 15 min. incubation. The extension of incubation time was found unnecessary since it does not improve the efficiency of extraction.

The temperature of the water bath (ranging from 70°C to boiling) showed no significant influence on extraction, so all subsequent experiments were performed at 70°C.

Separation of the water phase and SRP was done after 1 h cooling of the samples in freezer. Preliminary experiments showed that when residual sample solution was separated by the surfactant rich phase by simple decanting, essential decrease of analyte signals was observed. Pipetting the upper phase of aqueous solution allows more precise and reproducible separation, without analyte loss. After separation, the viscous SRP was dissolved with 1 mol L^{-1} HNO_3 up to 4 mL final volume. Hence, a preconcentration factor of 10 is obtained for the developed CPE procedure of lanthanides with enaminone.

Comparison of CPE procedures with both ligands 3-etylamino-but-2-enoic acid phenylamide and 8-hydroxyquinoline

The new CPE system for extraction of lanthanides with 3-etylamino-but-2-enoic acid phenylamide (En) was compared to a published CPE method with a well-known ligand 8-hydroxyquinoline (8-HQ) [12]. The comparison was made in three aspects: 1) affinity towards target lanthanides; 2) co-extraction of concomitant elements; and 3) potential spectral interferences caused by co-extracted elements. For these reasons, extraction was performed under optimal conditions for both ligands with standard solution of lanthanides (Ln 1 µg L^{-1}), and with the same solution spiked with multielement standard (MY) containing 28 elements in concentration 10 µg L-1.

When lanthanides only are subjected to the optimized CPE procedures both ligands show high affinity towards them (Figure 2).

The tested enaminone shows better results, allowing to achieve quantitative recoveries, while the efficiency of the reaction with 8-HQ is lower (R=71-94%).

Both ligands were compared also when the model solution of multielement standard with concentration 10 µg L^{-1} are subjected to CPE procedures (Figure 3). The experiment showed that alkali and alkaline earth elements are not extracted in both CPE systems. The recoveries for Na, K, Mg and Ca are less than 5%, so they are not shown in the graph. The extraction degree of Ba is also very low (~5%), but it needs special attention because the most significant risk of spectral interference on lanthanide isotopes is due to the formation of polyatomic barium ionic species as hydrides, oxides, and hydroxides.

8-hydroxyquinoline, as a broad spectrum ligand binds most of the elements in the soliton. Its high affinity to Al is due to the formation of well-known compound Tris (8-hydroxyquinolinato) aluminum. Comparative extraction efficiency for both ligands is observed for Cu, Zn, Cr, and Bi.

3-etylamino-but-2-enoic acid phenylamide extracts most of the concomitant elements in lower degree (V, Mn, Fe, Co, Ni, Mo, Ag, and Ba). Only for Pb, the tested enaminone shows higher efficiency than 8-hydroxyquinoline.

In this comparison, 3-etylamino-but-2-enoic acid phenylamide shows better selectivity than 8-HQ, which could be an advantage of the new compound in case of complicated matrices with high concentrations of metals.

Co-extracted elements could worsen the overall performance of the proposed method for lanthanide preconcentration in two aspects: the depletion of ligand could decrease the recovery for analytes and/or the presence of elements in final solution could provoke spectral interferences on selected lanthanide isotopes.

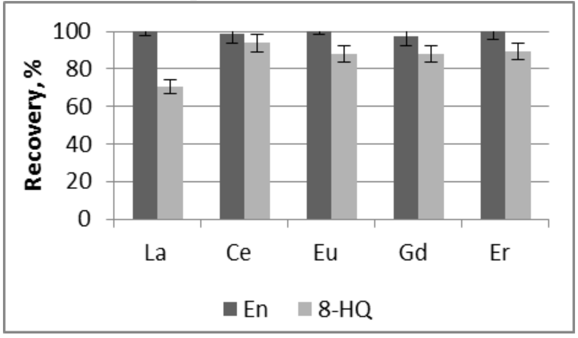

Figure 2. Analytical recovery for lanthanides after CPE with 8-HQ и En; optimal conditions for each ligand.

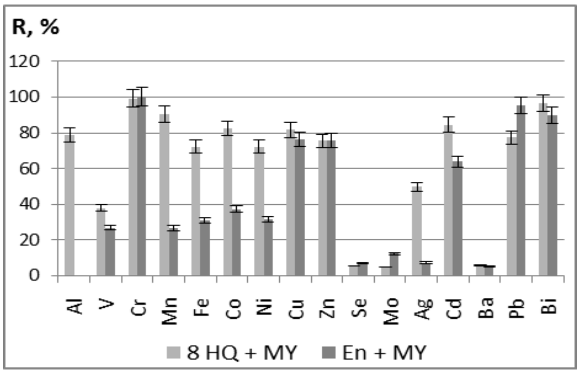

Figure 3. Recovery for concomitant elements (C=10 µg L^{-1}) after CPE with 8-HQ and En.

To study both effects, model solutions of lanthanides only and lanthanides mixed with multi-elemental solution were subjected to the optimized CPEs. In all cases, the concentration of lanthanides was one order of magnitude lower than other elements (1 and 10 µg L^{-1} respectively). Isolated SRPs were diluted and measured by ICP-MS. Figures 4 and 5 show signals for two isotopes per element (with exception of La) after extraction with 3-etylamino-but-2-enoic acid phenylamide and 8-hydroxyquinoline respectively in the presence and absence of multi-elemental solution.

When the CPE is performed with enaminone, the signals for all tested isotopes are statistically identical independently on the presence of co-extracted elements (Fig. 4) This is evidence that the extraction of target Ln ions is not deteriorated by the concomitant metal ions even if their concentration is higher by 1 order of magnitude. In addition, comparable signals for the two series showed that co-extracted elements do not provoke spectral interference.

When the CPE is performed with the classical reagent 8-hydroxiquinoline, the signals of extracted lanthanides in the presence and absence of concomitant elements are statistically indistinguishable again, with exception of ^{139}La (Fig. 5). The minor increase of average values in the presence of multi-elemental solution is an indication for possible spectral interferences when the content of co-extracted elements in a real sample exceeds too much this of tested lanthanides.

The most significant difference is observed for ^{139}La. It should be noted that the only other isotope of ^{138}La (natural abundance, NA=0.09%) could not be measured because of strong isobaric overlap originated by two other elements: the main isotope of barium (^{138}Ba, NA= 71.7% and co-extraction ~5%) and ^{138}Ce (NA=0.25%, extraction ~94%). It can be seen from Figure 2 that the extraction degree of La with 8-HQ is the lowest among examined lanthanides (R=71%). The observed enhancement in the presence of multi-elemental solution could be due to the synergistic effect originated by the formation of mixed complexes. There are investigations proving that lanthanides are capable of forming some mixed complexes with transition metals such as Co, Ni and Mn [25]. As can be seen from our previous investigations, the extraction degree of these elements with 8-HQ is much higher in comparison to tested enaminone (Fig. 3).

Analytical performance

Both sensitivity and limits of detection of ICP-MS method are highly dependent on natural abundance of selected isotope. Therefore, the final method includes the isotopes free from isobaric overlap of examined lanthanides which are more abundant - ^{139}La, ^{140}Ce, ^{153}Eu, ^{157}Gd, ^{166}Er.

Non-spectral matrix effect generated by the surfactant phase diluted in the final solution was studied. It was established that the high concentration of surfactant causes suppression of the signals for all tested elements (from 16% for Er up to 22% for La) in comparison to water standards.

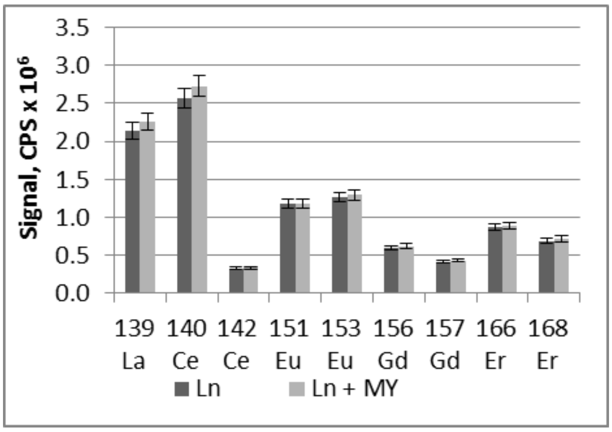

Figure 4. Signals for lanthanides after CPE in presence (Ln + MY) and absence (Ln) of concomitant elements; used ligand - En.

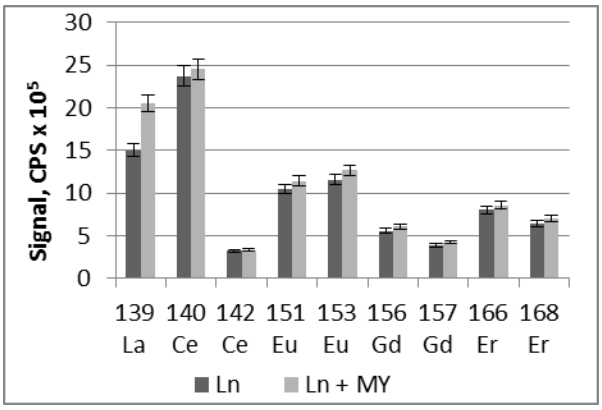

Figure 5. Signals for lanthanides after CPE in presence (Ln + MY) and absence (Ln) of concomitant elements; used ligand - 8-HQ.

Therefore it is recommended that all calibration standards must be subjected to the CPE procedure together with the analyzed samples.

Furthermore, typical for ICP-MS sensitivity drift was also observed although the instrument was conditioned by 20 minutes aspiration of diluted surfactant solution (10% TX-100). Since the signal drift was similar for all analytes, it was assumed that it is due to a change in sample transport and aerosol generation. Several elements were tested as IS candidates (Ge, Rh, In, Te, Re and Tl) in order to overcome this effect. Re was selected as the most appropriate one.

The analytical figures of merit for the CPE procedure for lanthanides with 3-ethylamino-but-2-enoic acid phenylamide as a new ligand are presented in Table 1. Procedural calibration was made by 4 standard solutions and a blank passed through CPE in concentration range 0.05-5 μg L^{-1} with preconcentration factor of 10. Good coefficients of determination (R^2>0.9972), together with low standard deviations obtained for the calibration slopes, are evidence for the reproducibility of the procedure. Limits of detection (LOD) for all elements are calculated as the concentration, equivalent to three standard deviations of the blank sample (n=5), divided by the corresponding slope of procedural calibration.

Analysis of certified reference material and application

Accuracy of the procedure is proved by analysis of certified reference material for surface water SPS Quality Level 1. Obtained data is presented in Table 2. Analytical recovery was in the range 94-108% and all measured concentrations are statistically identical with the certified values. This good coincidence is clear evidence for the accuracy of the procedure. It should be mentioned that barium is also present in the reference material (in concentration 50 μg L^{-1}) and the obtained results are an indication for effective separation of lanthanides from interfering element by CPE procedure with enaminone.

The CPE procedure was applied for determination of lanthanides in real water sample and results are shown in Table 2. For approval of adequateness of the procedure, samples were spiked with analytes. Recoveries of spiked lanthanides at two levels (100 and 500 ng L^{-1}) were in the range 97-104% for all studied elements (Table 2).

Table 1. Analytical figures of merit obtained by measuring 5 calibration standards passed through the extraction procedure. Standards concentration – 0, 0.05, 0.1, 1, 5 μg L^{-1}; internal standard ^{185}Re; Preconcentration factor of 10.

	Slope, (cpsLn cpsIS^{-1} Lμg Ln^{-1})	**SD slope**	**Intercept, (cpsLn cpsIS^{-1})**	**SD intercept**	**R^2**	**LOD, ng L^{-1}**
^{139}La	1.09	0.02	-0.2	0.5	0.9976	1.3
^{140}Ce	1.32	0.02	-0.4	0.5	0.9982	0.4
^{151}Eu	0.60	0.01	-0.2	0.3	0.9972	0.2
^{157}Gd	0.32	0.01	-0.1	0.1	0.9977	0.6
^{166}Er	0.45	0.01	-0.2	0.2	0.9975	0.2

Table 2. Certified and measured concentration for lanthanides (μg L^{-1}) after CPE with 3-Ethylamino-but-2-enoic acid phenylamide in certified reference material for surface water – SPS quality Level 1, with corresponding uncertainty (U) estimation: * Expanded instrumental uncertainty; ** Uncertainty given in the certificate; Results obtained for lanthanides in real water (ng L^{-1}) sample and R% - recovery of spiked samples.

	Meas., μg L^{-1}	**U, k=2***	**Cert., μg L^{-1}**	**U****	**Water 1, ng L^{-1}**	**U, k=2***	**R, % spike 100 ng L^{-1}**	**R,% spike 500 ng L^{-1}**	**Water 2, ng L^{-1}**	**U, k=2***
La	0.52	0.01	0.50	0.01	68	1	103±1.3	97±1.6	130	10
Ce	0.47	0.03	0.50	0.01	2	0.1	104±0.5	97±1	780	20
Eu	0.52	0.03	0.50	0.01	1	0.2	98±1	95±1.2	390	20
Gd	0.49	0.02	0.50	0.01	1	0.4	102±1.2	101±0.5	2100	30
Er	0.49	0.02	0.50	0.01	2	0.2	98±1.2	99±2.4	420	10

CONCLUSIONS

The proposed procedure for CPE with 3-ethylamino-but-2-enoic acid phenylamide shows high potential for determination of lanthanides in complex environmental samples. The ligand is more selective than classical compound 8-hydrohyquinoline used for separation of lanthanides. The effective separation of lanthanides from concomitant barium by developed CPE method allows eliminating of spectral interferences. Obtained limits of detection with preconcentration factor of 10 are satisfactory for examination of real waters samples.

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ЕКСТРАКЦИЯ ПРИ ТЕМПЕРАТУРА НА КОАГУЛАЦИЯ НА ЛАНТАНИДИ ОТ ВОДНИ ПРОБИ С 3-ЕТИЛАМИНО-БУТ-2-ЕНОВА КИСЕЛИНА ФЕНИЛАМИД И ICP-MS АНАЛИЗ

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(Резюме)

Изследван е нов лиганд от клас енаминони за екстракция при температура на коагулация на лантаниди (La, Ce, Eu, Gd, Er) от водни разтвори. Оптимизирани са екстракционните параметри: pH на водната фаза, температура и време на нагряване, вид и количество на използваното повърхностно активно вещество. Концентрацията на аналитите е определена чрез ICP-MS, след подходящо разреждане на ПАВ-обогатената фаза. Екстракционната система с новия лиганд притежава висока ефективност за разделяне на лантаниди от съпътстващите алкални и алкалоземни елементи, което значително понижава риска от спектрални пречения при анализ на реални проби. Селективността на изследвания енаминон е сравнена с тази за 8-хидроксихинолин. Инструменталният дрейф на чувствителността е коригиран с вътрешен стандарт рений. Оптимизираната процедура е приложена за анализ на сертифициран референтен материал вода и реални проби. Получените граници на откриване са в интервала 0.02-0.13 ng L^{-1}, при фактор на концентриране ФК=10.

Ключови думи: Лантаниди, Екстракция при температура на коагулация, Енаминони, ICP-MS, Анализ на води