

# Positive/Negative Liquid Secondary Ion Mass Spectrometry of *Ln-EDTA* (1:1) Complexes Formation of Molecular Ion Adducts with Neutral Species of the Matrix or *Ln-EDTA*

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**Summary.** The mass spectra of 1:1 complexes of *EDTA* with lanthanide cations ( $Ln = \text{Sm, Eu, Gd, Tb or Dy}$ ) upon positive/negative LSIMS are presented. In glycerol used as a matrix, adduct-ions such as  $[M+H]^+$ ,  $[M+H+nGly]^+$ ,  $[2M+H]^+$ ,  $[2M+H+Gly]^+$  (positive LSIMS) or  $[M-H]^-$ ,  $[M-H+nGly]^-$ ,  $[2M-H]^-$ ,  $[2M-H+Gly]^-$  (negative LSIMS), where  $n = 1-3$ , are formed. Reactions leading to the formation of adduct-ions are suggested.

**Keywords.** *Ln-EDTA* complexes; Liquid secondary ion mass spectrometry; Matrix effect.

**Positive/negative Liquid-Sekundärionen-Massenspektrometrie von *Ln-EDTA*-(1:1)-Komplexen.  
Bildung von molekularen Ionenaddukten mit neutralen Spezies aus der Matrix oder *Ln-EDTA***

**Zusammenfassung.** Die Massenspektren von 1:1-Komplexen von *EDTA* mit Lanthanidenkationen ( $Ln = \text{Sm, Eu, Gd, Tb oder Dy}$ ) mittels positiver/negativer LSIMS werden präsentiert. In Glycerin als Matrix bilden sich Adduktionen wie  $[M+H]^+$ ,  $[M+H+nGly]^+$ ,  $[2M+H]^+$ ,  $[2M+H+Gly]^+$  (positive LSIMS) oder  $[M-H]^-$ ,  $[M-H+nGly]^-$ ,  $[2M-H]^-$ ,  $[2M-H+Gly]^-$  (negative LSIMS), wobei  $n = 1-3$ . Es werden Reaktionen vorgeschlagen, die zur Bildung von Adduktionen führen.

## Introduction

The complexes of ethylenediaminetetraacetic acid (*EDTA*) with a large number of metal cations [1, 2] as well as those with lanthanides [3, 4] have been well-known in the analytical chemistry for several decades.

In the field of the spectroscopic study, we already reported fluorescence properties of some lanthanides with acetylaceton (*acac*) [5–9] and aminopolyacetic acids (*EDTA*, *NTA* and *IDA*) [10–16]. In addition, *acac* complexes with the whole family of the lanthanides were characterized using the electron impact mass spectrometry (EIMS) [17]. However, the application of electron impact ionization to examine *Ln-EDTA* complexes was proven unsuccessful. Under EI conditions the thermal process was found to decompose totally the studied complexes [18].

Since the early 1980s, the fast atom bombardment (FAB) [19–21] or liquid secondary ion mass spectrometry (LSIMS) [22], have been successfully used in organometallic and coordination chemistry (see reviews [23, 24]).

An application of a liquid matrix is the essential part of FAB or LSIMS. A number of compounds have been examined and discussed as matrixes [25–27]. In our study, the LSIMS of some *Ln-EDTA* complexes in glycerol matrix was examined. Although we carried out the investigation on the 1 : 1 *EDTA* complexes with Sm, Eu, Gd, Tb and Dy only, their behaviour should be typical of the whole series of lanthanides.

## Experimental

The positive/negative liquid secondary ion mass spectra were recorded on a two sector Varian MAT 731 mass spectrometer combined with a Teknivent Vector/One Workstation. A CsI gun supplied the primary-ion beam (6–8 kV, Cs<sup>+</sup>). The secondary ion beam was accelerated to 8 kV. Samples were dissolved in water (1 µg/µl) and the solution was mixed with glycerol (1 : 1). 1.0 µl of the mixture was deposited on a stainless steel target (60° angle of incidence, 5.7 mm<sup>2</sup> surface).

The samarium, europium, gadolinium, terbium, and dysprosium 1 : 1 complexes with ethylenediaminetetraacetic acid were prepared according to the method described previously [28].

**Table 1.** Positive/negative LSI mass spectra of Sm, Eu, Gd, Tb and Dy 1 : 1 complexes with *EDTA*

LSIMS	Formula	Relative intensities (%)				
		Sm <sup>a</sup>	Eu <sup>a</sup>	Gd <sup>a</sup>	Tb <sup>b</sup>	Dy <sup>a</sup>
Positive	$[M+H]^+$	48	38	29	28	40
	$[M+H+nGly]^+$					
	<i>n</i> = 1	100	100	100	100	100
	<i>n</i> = 2	33	31	30	22	15
	<i>n</i> = 3	12	19	17	9	5
	$[2M+H]^+$	25	22	13	4	18
	$[2M+H+Gly]^+$	17	12	10	1	5
Negative	$[M-H]^-$	100	100	100	100	100
	$[M-H+nGly]^-$					
	<i>n</i> = 1	38	29	41	32	27
	<i>n</i> = 2	18	10	20	10	6
	<i>n</i> = 3	6	3	7	3	1
		$[2M-H]^-$	22	23	14	2
	$[2M-H+Gly]^-$	5	3	4	-	2

<sup>a</sup> Relative intensities of the ions with regard to <sup>152</sup>Sm, <sup>153</sup>Eu, <sup>158</sup>Gd and <sup>164</sup>Dy isotopes, when the ion contains only one atom of lanthanide; the most intense peak of the appropriate cluster is given for dilanthanide-ions

<sup>b</sup> Monoisotopic, relative intensities with regard to <sup>158</sup>Tb

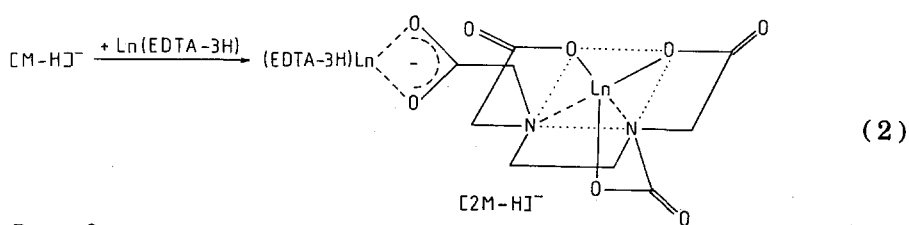
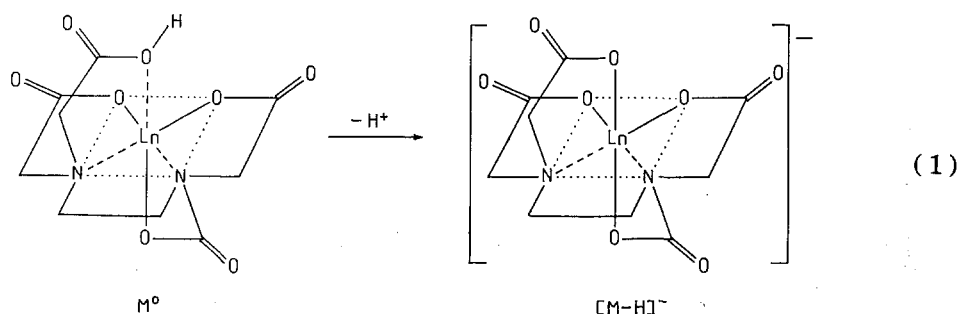
## Results and Discussion

In all the investigated complexes, protonated molecular ions  $[M+H]^+$  in the positive spectra, or deprotonated  $[M-H]^-$  ions in the negative LSIMS were present. In addition, the adduct-ions of formulae  $[M+H+nGly]^+$ ,  $[2M+H]^+$  and  $[2M+H+Gly]^+$  in the positive mode of ionization as well as  $[M-H+nGly]^-$ ,  $[2M-H]^-$  or  $[2M-H+Gly]^-$  ions in the negative one, were also observed. Positive/negative mass spectra of the complexes are summarized in Table 1.

### Formation of the Adduct Ions in the Negative LSIMS

Deprotonated molecular  $[M-H]^-$  ions are formed as a result of the detachment of a proton from the carboxyl group, as shown in Reaction (1).

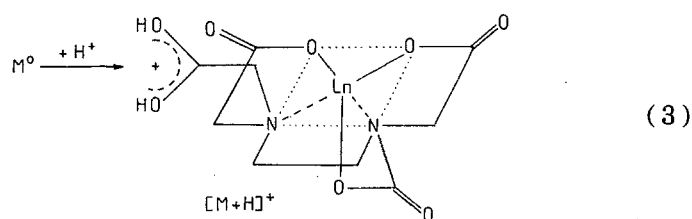
The presence of the series of adduct-ions with glycerol of the formula  $[M-H+nGly]^-$  ( $n=1-3$ ) as well as of another adduct,  $[2M-H]^-$ , is observed. The latter is formed by the attachment of a neutral complex molecule to the  $[M-H]^-$  ion, as shown in Reaction (2). Its adduct with glycerol,  $[2M-H+Gly]^-$ , is also seen.



### Formation of the Adduct Ions in the Positive LSIMS

Attachment of a proton to the carboxyl group of the neutral molecule of the complex leads to the formation of  $[M+H]^+$  molecular ion, as shown in Reaction (3).

In negative LSIMS, the peaks corresponding to  $[M-H]^-$  ions were the most intense. The intensities of  $[M+H]^+$  ions are distinguishably lower than those of  $[M+H+Gly]^+$ . The plots of relative intensities of  $[M-H+nGly]^-$  and  $[M+H+nGly]^+$  ions ( $n=0-3$ ) are shown in Fig. 1.



React (2)

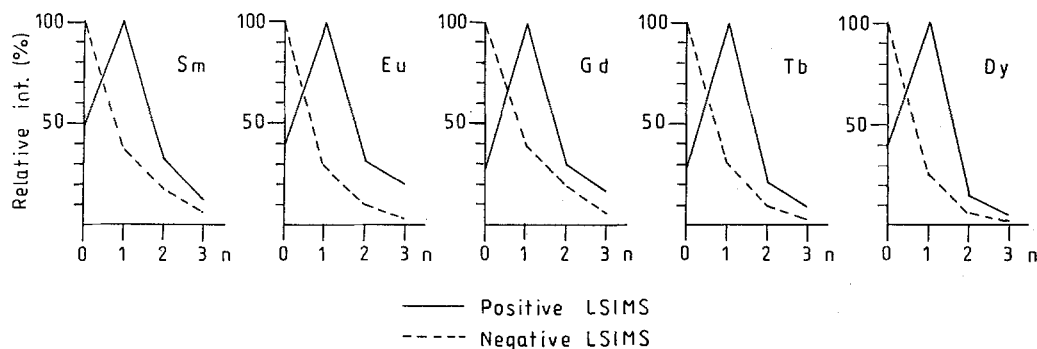
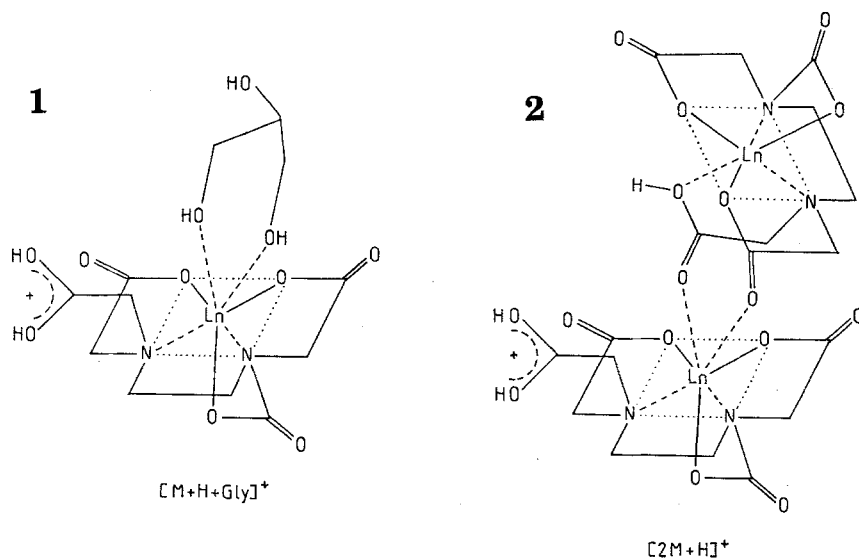


Fig. 1. Plots of the relative intensities of  $[M-H+nGly]^-$  and  $[M+H+nGly]^+$  ions

The plots of the intensities of molecular ion-adducts with glycerol show that the binding of glycerol to molecular ions is distinctly more favourable in the positive LSIMS than in the negative ones. In general, this binding is affected by the density of electrons which is lower in the positive ions than in the negative ones. As a result, glycerol via two O-Ln coordination bonds can easily form an additional six-membered ring with the  $[M+H]^+$  ion. Its polycyclic structure is shown in Formula 1.

Another adduct,  $[2M+H]^+$ , can be formed via the attachment of the neutral molecule of the complex to the  $[M+H]^+$  ion. Coordination bonds binding the



neutral molecule to the ion can be formed between carbonyl-oxygens of the neutral *EDTA* moiety and the lanthanide of the  $[M + H]^+$  ion as well (Formula 2).

When instead of  $[M + H]^+$ , the  $[M + H + Gly]^+$  ion is involved in this process, ions of the formulae  $[2M + H + Gly]^+$  can be formed.

### Conclusions

The formation of all adduct-ions discussed in the text may be concluded to be associated with the electroacceptable nature of lanthanides. The acceptance of lone electron pairs by the central atom of the complex may be improved by the formation of additional coordination Ln-O bonds between ions formed upon LSI and neutral species of *EDTA* or the matrix. In the latter case, the effectiveness of glycerol-binding is significantly increased by the formation of an additional six-membered glycerol ring with the lanthanide.

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