Journal of Chromatography A, 1272 (2013) 26–32

Contents lists available at SciVerse ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

High performance ion chromatography of transition metal chelate complexes and aminopolycarboxylate ligands

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ARTICLE INFO

Article history:
Received 4 September 2012
Received in revised form
19 November 2012
Accepted 21 November 2012
Available online 29 November 2012

Keywords:
Ion chromatography
Transition metal chelate complexes
Chelating ligands
Secondary chemical equilibria
Interconvertible forms of complexes
Probability density function for chromatograms

ABSTRACT

A simple ion chromatographic method was developed for the separation of transition metal chelates (CuEDTA, CuDCTA, ZnEDTA, ZnDCTA) and free anionic complexing ligands (EDTA, DCTA) using alkaline carbonate eluents and conductivity detection. The complex equilibria and kinetic process of separations were studied in order to understand major factors in the control of selectivity and retention order of complex anions. A systematic study was applied to identify the additional peaks of the system as $NaEDTA^{3-}$, $NaHEDTA^{2-}$, Na_2EDTA^{2-}, $EDTA^{4-}$/$HEDTA^{3-}$, $DCTA^{4-}$/$HDCTA^{-3}$. On the basis of microequilibrium considerations of chelating ligand, it was shown that one should expect the peaks of sodium chelates when the ligand is in excess in the sample solution. The probability density function was introduced for calculation of complex chromatograms, because complexing ligands can exist in at least two different interconvertible forms in the presence of metal ion. The chromatogram of interconverting chelate species can be given as the sum of probability density functions (P) weighed by the molar fractions of complexed (Φ_{ML}) and dissociated (Φ_L) forms. The influences of kinetic rate of complex formation and dissociation on the distribution of components between eluents and ion exchange stationary phases were quantitatively described and demonstrated by elution profiles. The applicability of the developed method is represented by the simultaneous analysis of transition metal chelates and inorganic anions. ICP-AES analysis and FTIR-ATR technique were used for confirmation of IC results for metals and ligands, respectively. Collection protocols for the heart-cutting procedure of chromatograms were applied in the analysis of target components. The limit of detection and linearity of the method in the range of 0.01–0.25 mM sample concentration were also presented.

1. Introduction

The variability of the eluent composition with complexing agents can be used to exploit a wide range of secondary chemical equilibria and thereby obtain a very broad scope for ion-chromatography. One of the effective developments that have been made in ion chromatography in the past decade is the introduction of a procedure, which allows the simultaneous analysis of metal cations and simple anions [1,2] as well as weak aliphatic organic acids. Our previous papers [3,4] have indicated the usefulness of a complexing retention model in controlling solute retention behaviors and in improving the selectivity of this separation system. The theory is based on the extension of ion-exchange equilibrium by protonation and complex formation equilibria [3]. Practical application of this model to the determination of the elution behavior of complexed species proves and demonstrates the reliability of the method.

Free vs. bound metal is often a key piece of information in environmental and biomedical studies. However, the simultaneous determination of trace metals and multidentate chelating agents remains one of the challenging areas of analytical separation. The system that contains several ionic species in the eluent and different forms of analytes in the sample is rather complicated. Renewed interest in these separations has recently sparked the method development for both the complexed and competitive polyvalent ligands. One promising example is the use of high performance anion chromatography for the separation of metal chelates including different metals and different aminopolycarboxylate ligands as target analytes.

The ethylene-diaminetetraacetic acid (EDTA) and the trans-1,2-diamine-cyclohexane-tetraacetic acid (DCTA) are strong chelating agents able to form sufficiently stable chelates with different metal ions. The aminopolycarboxylic acids, due to their high complexing ability have a variety of applications in analytical chemistry, nuclear medicine, chelation therapy, water analysis [5] and they interact in many biological active systems [6], geological materials. These ligands form water-soluble complexes with most transition and heavy metals, which may result in the contamination of soils

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http://dx.doi.org/10.1016/j.chroma.2012.11.054

[7]. They can remobilize metals in nature and may cause release into ground water and their uptake by plants [8]. Degradation of chelating agents is controversial, but it is known that EDTA is not likely to biodegrade easily in nature.

Because aminopolycarboxylic acids are also a potential risk to the environment, it is important to develop a selective analytical technique for their simultaneous determination with metals. Selective method is needed that is not adversely affected by inorganic ions and organic matter in a variety of matrices. In addition, identification of ligands is difficult because any change in sample could change the complex equilibria and coordination of analytes. Several MS friendly separation methods in which ICP/MS [9] and LC/MS/MS [10] were used to determine metals and chelating ligands have been published in the literature. It is a possible future direction, however the cost and complexity for routine analysis is currently high. For GC method the main drawback is the need to perform a derivatization step of chelating ligands prior to analysis. It is also a labor-intensive and multistep procedure [11]. Separation of a number of transition metal complexes as HEDTC chelates by micellar electrokinetic capillary chromatography and pre-capillary complexation with direct photometric detection was investigated [12]. In recent years, there has been increasing interest in the separation of transition metal ions using surface bonded chelating groups. Some excellent and useful methods related to these topics (wall-coated CE, CEC and chelation ion chromatography) have attracted special attention [13,14]. The resultant chromatographic systems have ability to separate metals with unique selectivity, whilst different free ligands cannot be separated.

The aim of this paper has been to develop a simple and extended ion chromatographic method based on a systematic retention study and complex formation equilibria of transition metal chelate complexes with EDTA and DCTA ligands. Although it has been accepted that ion exchange is the main retention mechanism, secondary chemical interactions – such as protonation, complex forming and kinetic process – can play a significant role in this system, leading to changes in selectivity. The complexing ligand as anion, being added to the sample also moves through the column and appears often as multiple or pseudopeak. It is therefore essential to understand the mechanism and control of separation parameters. Our primary focus was to examine theoretically and also practically the additional peaks and kinetic aspects of complex systems. Insights will help improve the qualitative information on the complex species of interest. ICP-AES analysis and FTIR-ATR technique were also used for peak identification and thus provide the confirmation of IC results.

2. Theory

2.1. Complex formation and ion-exchange equilibria of metal chelates

By the means of chelation ion chromatography, ligands as anions and metals as anionic complexes can be separated in a single chromatographic run. Polydentate complexing anions, such as aminopolycarboxylic acids (EDTA, DCTA, etc.), tend to form stable chelate complexes with most of the di- and trivalent metal cations at alkaline pHs. When basic solution contains an excess of strong complexing anion of high charge, metal ions will occur as anionic complexes and can be separated by anion exchange. Hence this method provides simultaneous metal and anion separation. The resulting complexes may have a net charge, depending on the nature of the species involved in the complex formation and the conditions used:

$$L^{n-} + M^{m+} \overset{\beta}{\rightleftharpoons} [ML]^{z-} \quad (1)$$

where L^{n-} represents a polydentate complexing ligand, M^{m+} a metal cation, $[ML]^{z-}$ the formed chelate complex, and z is the net charge of it ($z = m - n$). The ion-exchange equilibrium between the eluent and the chelate anions may be given by the following:

$$zR - E + [ML]^{z-} \overset{K_{ML/E}}{\rightleftharpoons} R_z - ML + zE^{-} \quad (2)$$

where R represents the positively charged ion-exchange functional group of the stationary phase, E^- is the anion of the eluent competing with the chelate during the elution process, and $K_{ML/E}$ the ion-exchange equilibrium constant of the above reaction. An advantageous condition of the method is that the similar alkaline pH-range (9–11) is favourable to the stability of the metal complexes and also to their elution in anionic form.

Depending on the pH of separation, the protonation of the coordinated ligand as a side reaction can occur:

$$[ML]^{z-} + H^{+} \overset{K_H}{\rightleftharpoons} [MHL]^{(z-1)-} \quad (3)$$

If z is larger than 1, the protonated chelate has also a net negative charge and can be separated on anion exchanger, as well.

$$(z-1)R - E + [MHL]^{(z-1)-} \overset{K_{MHL/E}}{\rightleftharpoons} R_{(z-1)} - MHL + (z-1)E^{-} \quad (4)$$

Accordingly, several factors affect the separation of chelate anions on anion exchanger. These are the complex formation [Eq. (1)], ion-exchange equilibria [Eqs. (2) and (4)] and protolysis [Eq. (3)]. Note, that depending on the rate of the latter process, the protonated and dissociated complex may or may not be separated (see Section 2.2) by means of anion chromatography.

If more than one chelate ligand is present at the same time it is also possible for metals to form complexes that involve more than one ligand. In summary, the charge of components, kinetic rate and chemical equilibria of complex forming as well as the eluent composition play vital parts in retention of complex solutes.

2.2. Kinetic aspects of separation of interconverting chelate anions

As could be seen in the previous section, polydentate complexing ligands can exist in at least two different interconvertible forms in the presence of metal ion [complexed ML^{z-} and free L^{n-}, see Eq. (1)], and both forms undergo the usual chromatographic exchange between the mobile and stationary phases. Eq. (5) shows the scheme of interconversion (complex formation and dissociation) of ionic $EDTA^{4-}$ and $[MEDTA]^{2-}$ species and the distribution of these species between the alkaline mobile phase and the pellicular anion exchanger.

$$\begin{array}{ccccc} MEDTA_M^{2-} & \underset{k_c^M}{\overset{k_d^M}{\rightleftharpoons}} & EDTA_M^{4-} & + & M_M^{2+} \\ \uparrow\downarrow & & \uparrow\downarrow & & \uparrow \\ MEDTA_S^{2-} & \underset{k_c^S}{\overset{k_d^S}{\rightleftharpoons}} & EDTA_S^{4-} & + & M_S^{2+} \end{array} \quad (5)$$

where S and M superscripts denote the stationary- and mobile phases, k_d and k_c represent the rate constants of complex formation and dissociation, respectively.

Accordingly, the shape of chromatogram registered at the outlet of the column depends much on the rate of dissociation (r_d) and complex formation (r_c) of that compound. Note, that both r_d and r_c are proportional to the concentrations of the reactants and the appropriate rate constants (k_d or k_c).

The chromatogram of interconverting EDTA species can be given as the sum of probability density functions (P) weighed by the