

## Stability and Structural Characterization of Chelated Fertilizers

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**Abstract** In recent years, agricultural intensification and the need for reduced fertilizer application have rendered soil remediation and agricultural non-point-source pollution control globally significant. Compared to inefficiently utilized inorganic salt fertilizers, chelated fertilizers are more efficient and environmentally friendly, and have thus attracted considerable attention. In the new international context, more attention is being paid to soil remediation and reductions in agricultural non-point-source pollution, as the demand for high-quality agricultural products increases. Chelating fertilizers may play important roles in these contexts; models of stability and structure are required to provide both the theoretical basis for further development and data supporting continuing research and development. The stability constant reflects the stability of a chelated material; the stability constants of chelates can be calculated mathematically using the generating, Leden, and/or Fronaeus function (s). Although no standard method is yet available for the determination of stability constants, a great deal of relevant work has been performed worldwide. However, most methods are not yet mature, and appropriate stability constant reference values remain controversial. Since most of the fertilizers analyzed used amino acids for chelation, other ligands hardly received attention, potential applications of other ligands should be fully exploited. The molecular structure of a compound determines its properties. Structural characterization contributes to the qualitative analysis of chelated fertilizers, improves the understanding of experimental phenomena, and affects the selection of detective methods. The first consideration is whether the chelate is pure. Even if the levels of impurities are low, reliable structural data can be difficult to obtain. Therefore, we systematically summarize progress in how chelated fertilizer stability is assessed and how such fertilizers are structurally characterized. We focus on the advantages and disadvantages of various processes, outlining the need for future research. And we provide a theoretical basis for the development and effective utilization of chelated fertilizers.

**Keywords** Chelated fertilizer; Stability constant; Chelate strength; Structural characterization

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### Introduction

Chelated fertilizers are compounds with pincer-shaped ring structures bearing ligands such as amino acids, polypeptides, sugars, ethylene-diamine tetra-acetic acid (EDTA),

and humic acid that complex the metal elements required by plants; the ligands also form co-ordination bonds with the metal elements. Currently, the most common trace element fertilizers used worldwide are inorganic salts. Such fertilizers, applied alone or as mixtures, are easily fixed by the soil, rendering absorption and utilization by plants difficult. Moreo-

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ver, trace elements that differ in terms of their inorganic salt forms may exert significant mutually antagonistic effects, reducing the efficiency of fertilizer utilization. Today, large-scale applications of nitrogen, phosphorus, and potassium fertilizers are increasing the replanting indices of farmland, and the levels of trace elements removed from soil by harvested crops are continuously rising, reducing the background levels of such elements in some soils, even triggering soil degeneration. In contrast, the biochemical stability of chelated metals eliminates antagonistic effects among nutrients, thus improving plant nutrient-deficiency symptoms. Therefore, the proportions of metal-chelating fertilizers should be increased to comply with current rules on crop characteristics.

Early in the development of chelated fertilizers, the chelating agents used were principally EDTA<sup>[1]</sup> and citric acid<sup>[2]</sup> and sugar alcohol<sup>[3]</sup>. However, these agents are expensive and thus unsuitable for widespread agricultural application. Humic acid<sup>[4-5]</sup> is a cheaper but less effective chelator. Amino acids, polysaccharides, peptides, and proteins are chelators used to sequester trace elements and increase levels of organic matter. However, the raw materials most often used to produce amino acid chelators are derived from livestock and poultry feathers, which may lead to problems with heavy metals and organic pollution. Also, the complexing ability of the chelating agent directly affects fertilizer quality. For example, EDTA is a strong chelator, compromising metal release and absorption by plants; metals may accumulate in the environment, even triggering anti-nutritional effects<sup>[6]</sup>. Thus, the fertilizer stability constant (or chelate strength) is of critical importance when attempting to improve a chelated fertilizer and better understand its mechanism of action. Also, although amino acids, polysaccharides, peptides, and proteins have all been used as chelating agents, most studies have evaluated amino acids only, and only in a qualitative manner; structural characterization of chelates is not yet mature. Thus, there is an urgent need to study, optimize, and combine various analytical techniques.

We searched the worldwide literature, and here summarize the methods used to measure chelate stability (or strength) and fertilizer structure. We put forward suggestions and prospects for future research directions and hope to provide a theoretical basis for further development of chelated fertilizers.

## 1 The stability constants (chelate strengths) of chelated fertilizers

During chelate fertilizer synthesis, stability is judged by measuring stability constants or chelation strengths. Analysis of the stability constants (chelate strengths) of chelated fertilizers

affords a theoretical basis that allows prediction of the release of organic substances from metal elements and ligands. Also, ion migration and active transport can be modeled, as can plant absorption and utilization rates. Currently, only qualitative characterization is possible, with a focus on stability (strong or weak); quantitative analyses are lacking. It is unclear how the stability constant (or chelating strength) affects plant absorption and utilization of metals. Therefore, chelate stability must be measured in combination with fertilizer effects (absorption and utilization by crops). Fertilizers that are stable and that chelate metals only moderately can thus be identified and synthesized.

### 1.1 Electrochemical methods

During chelate formation, changes in the concentrations of metal ions and ligands are accompanied by changes in electrochemical properties. Potentiometry, pH potentiometry, and polarography can be used to measure such changes. Potentiometry uses appropriate indicator and reference electrodes to form a battery, followed by measurement of electromotive force and calculation of the potential of the indicator electrode using the Fronaues function. However, the electrodes used must be reversible and inert. Also, the liquid junction potential affects the experimental data, creating erroneous deviations. pH potentiometry measures pH changes during chelate formation, and then calculates an equilibrium concentration and a ligand-generation function, and finally, a stability constant. The critical step in such a procedure is pH potentiometric titration. It is necessary to ensure the absence of metal hydroxide precipitation over the pH range chosen; the method cannot be applied if chelation is slow. In studies on mononuclear mixed complexes, pH potentiometry yielded reliable results. Furthermore, pH potentiometry can also be used to study complex multinuclear systems. Holwerda et al.<sup>[7]</sup> developed a parametric method to calculate chelation strength (a  $Q_i$  value) using complex equilibrium relationships and the half-wave potential differences ( $\Delta E$  values) between complexed and non-complexed metal ions, which can be derived polarographically. Stability constants were derived by reference to changes in the half-wave potentials of metal ions before and after the chelating agent was added. After reversible reduction of the metal ion polarographic wave, addition of a chelating agent caused the peak potential to shift in a negative direction as the ligand concentration rose. However, the method can be used only to determine the chelating strengths of organic trace elements in saturated solutions; the proportions of free and complex elements cannot be determined.

### 1.2 Spectrophotometry

Spectrophotometric methods measure changes in solution optical densities when chelates are formed, thereby indirectly measuring chelate stability. The stability constant of the com-

plex is usually measured using the equimolar continuous change method. Here, the concentration of one component is held constant, and the concentration of another component is varied. Changes in absorbance are then measured, and a formula is used to calculate the stability constant<sup>[8-9]</sup>. However, chelate stability and the coordination number greatly influence the results, which may be erroneous when the stability is too high (or low), or the coordination number is too high<sup>[10]</sup>. Spectrophotometry has been shown to be rapid and reliable when used to estimate the stability constants of complexes between copper and polyacrylic acid and has been widely used. However, if the complex is unstable, it is difficult to obtain an accurate absorption curve using the saturation method. More recently, some researchers developed a formula applicable to analysis of unstable complexes and used linear regression to calculate molar absorptivities and the extent of dissociation. Application of corrected molar absorbances and dissociation coefficients yielded more accurate stability constants. The method has been used to measure the stability constants of complexes containing calcium, magnesium, and barium. It is difficult to simultaneously measure the stability constants of multiple solution complexes, but a corresponding solution method has been developed<sup>[11]</sup>. However, the method has not been widely used because it is cumbersome, and data are difficult to derive. Double-color-point spectrophotometry<sup>[12]</sup> can be used to this end. Changes in the absorption spectra of two isochromatic materials are monitored (the equimolar continuous change method is used to obtain the first isochromatic, and a molar ratio method to obtain the second isochromatic). The molar absorptivities and equilibrium concentrations of the two substances are calculated based on the absorbances at two wavelengths, and stability constants are then obtained. In ultraviolet/visible spectrophotometry using the molar proportional method, the concentration of one component is held fixed, and that of another component is changed; absorbance changes are then measured. The relationship between absorbance and the composition of the solution is given by Lambert-Beer Law [ $A = \lg(1/T) = Kbc$ ], and the absorbance can thus be used to calculate ligand concentration<sup>[13]</sup>. The method is in general use and often yields satisfactory results. However, we encountered some difficulties when studying complex systems.

### 1.3 Other methods

Both electrochemical and spectrophotometric methods have certain limitations when used to determine the stability constants of complex chelates. Thus, liquid chromatographic and ion chromatographic, capillary electrophoretic, and dissolution approaches have been developed to deal with these problems. Liquid chromatography<sup>[14]</sup> effectively determines the stability constants of complex chelates, reverse-phase

chromatography<sup>[15]</sup> can be used to analyze complex chelates of metal ions with nucleotides or nitroso ligands, and ion chromatography can be employed to determine the stability constants of complexes formed between divalent cations and dicarboxylic acids. Capillary electrophoresis is widely used and is accurate and rapid. Stability constants have also been determined with the aid of affinity capillary electrophoresis<sup>[16]</sup>, combined with “mobility migration-constant”<sup>[17]</sup> and “ligand separation-constant” methods.

We summarize the principles, advantages, and disadvantages of the various methods in Table 1 below.

## 2 Structural characterization of chelated fertilizers

### 2.1 UV and fluorescence scanning

During chelate synthesis, the structures of the chelate and substrate differ; chelation development can be monitored by observing changes in the peak positions associated with maximum absorption. During the reaction, maximum peak absorption can even be used to assess the extent of chelation. Both ultraviolet and fluorescence scanning are commonly used to characterize aqueous chelate solutions. When the former method is employed, chelation changes the light-absorptive properties of the ligand, significantly shifting the absorption peak and allowing qualitative evaluation of chelate formation and its nature<sup>[18]</sup>. The principal ligand of the chelate is identified by reference to the peak absorption of that chelate. However, it is obviously essential to use ligands that absorb light in the near-UV region.

Ligands exhibiting different fluorescence excitation and emission spectra include the amino acids tryptophan, tyrosine, and phenylalanine. Fluorescence scanning is useful if such ligands are to be studied; chelate formation is often accompanied by changes in the locations and intensities of the fluorescent peaks. The addition of metal ions shifts the maximum absorption peaks, but high ion concentrations can trigger fluorescence quenching, reducing fluorescence intensities. Fluorescence spectrometry is applied in practical research; in one approach, it is applied in a comparative manner. For example, when whey protein-peptide and whey protein-peptide-calcium chelates are separately prepared at the same whey concentrations, fluorescence emission spectra in the range 300 ~ 500 nm can be used to explore chelation<sup>[19]</sup>. Another approach is to explore whether the fluorescence absorption peaks are offset and whether their intensities change, revealing the coordination bonds involved in chelation<sup>[20]</sup>.

### 2.2 Infrared spectroscopy

Infrared spectroscopy is a method of characterizing chelates based on comparison of chelating group status before and

**Table 1 Methods used to measure complex (chelate) stability constants**

Methods	Principle	Advantages	Disadvantages
Potentiometry	Using appropriate indicator and reference electrodes to form a battery, followed by measurement of electromotive force and calculation of the potential of the indicator electrode using the Fronaues function.	The method is simple, and the data is reliable. Applicable to complex systems of mixed complexes and multicore complexes. When the ligand is a macromolecular protein, this method is a better measurement.	The electrode used must be reversible and inert; Liquid junction potential affects the experimental data, creating erroneous deviations.
pH potentiometry	Measuring pH changes during chelate formation, and then calculates an equilibrium concentration and a ligand-generation function, and finally, a stability constant.	Easy to operate. The determination of mononuclear mixed complexes and complex multinuclear systems is very effective.	High pH requirement when measuring. Ensure the absence of metal hydroxide precipitation over the pH range chosen. Cannot be applied if chelation is slow
Polarography	The stability constants are derived by reference to changes in the half-wave potentials of metal ions before and after the chelating agent was added.	Widely used, and the method is gradually mature. No matter whether the metal ion reversible reduction reaction occurs at the electrode, the method can be applied.	The calculations are complex, and the ligand concentrations must be high. The coordination number must be controlled in order to get accurate results.
Iso-molar continuous variation method	The concentration of one component is held constant, and the concentration of another component is varied. Changes in absorbance are then measured, and a formula is used to calculate the stability constant.	Rapid and reliable. Wide selection of solutions. Suitable for low concentration solutions.	Difficult to measure the complex chelate system. The chelate stability and the coordination number greatly influence the results. High requirements for the mixing proportion.
Corresponding solution method	The average molar extinction coefficient is used to find the corresponding solution, and the stable constant is calculated according to the generating function.	Can be used for complex systems with multiple complexes in solution.	Finding the corresponding solution is difficult. Cumbersome, and data are difficult to derive.
Chromatography	The stability constant is calculated based on the retention time measured by chromatography.	Simple, rapid, high accuracy. Suitable for the determination of multi-order stepwise stability constant. Determination of variable complexes works well.	It is necessary to do a lot of work to determine the optimum separation conditions for different complexing systems. The chelate equilibrium movement occurs when the complex chelate system flows through the chromatographic column. The processing is complicated, and the technique is challenging.
Capillary electrophoresis	Ions or charged particles are driven by an electric field and separated in the capillary by mobility or apparent mobility.	Rapid determination and high accuracy. Can be used for complex system with low stability constant.	Cannot be used for slow chelation reaction determination; Cannot determine the chelating system formed with neutral ligands.

after complex formation. During chelation, ligand status changes, as do the characteristic absorption peaks<sup>[21-22]</sup>. Infrared spectroscopy can also be used to determine chelate conformation by analyzing harmonic vibration frequencies. The method is widely used in practice, usually in a comparative mode. The spectra of the chelate and precursors are com-

pared, and differences between telescopic vibrational frequencies and absorption peak positions and intensities are observed. For example, it is possible to determine whether carboxylic acids participate in coordination and how they do so by exploring the differences between the symmetric and asymmetric stretching vibrations of such acids. If a carboxylate ex-

hibits a value much smaller than  $160\text{ cm}^{-1}$  in the infrared spectrum, chelate coordination is in play. In general, metal ion chelation invariably changes the functional group, which is associated with informative changes in the positions of troughs and peaks<sup>[23]</sup>. However, such techniques require very pure ( $\geq 98\%$ ) crystalline samples; impurities cause absorption peaks to overlap, compromising comparisons and analyses. Of course, if an unknown sample is to be analyzed, the spectrum will be helpful, but other methods exploring chelate structure, such as ultraviolet/visible spectroscopy and nuclear magnetic resonance, will also be required.

### 2.3 Electron spin resonance (ESR)

Electron spin resonance spectroscopy distinguishes different paramagnetic species, simplifying complex spectra and identifying peaks. When using this technique, the electronic features of ligands must be first analyzed, followed by qualitative characterization of chelate coordination parameters<sup>[24-25]</sup>. This determines the extent of coordination at low pH. The method can be used to explore the effects of temperature and molar ratio on the coordination structure and its properties. However, it is difficult to apply valence bond theory during analyses, and only some types of substituents are amenable to analysis. Therefore, ESR usually serves only as a supplementary measurement of chelation. The technique has certain limitations. For example, when examining novel chelates of vanadyl (IV), it was necessary to use both X-ray diffractometry and ESR for precise analysis and structural simulation<sup>[26]</sup>.

### 2.4 X-ray diffraction

X-ray diffraction<sup>[27-28]</sup> by pure single crystals of chelates yields abundant structural information, especially in terms of symmetry. Purified chelates tend to be crystalline, with regular arrangements of particles. The crystal bond length, bond angle, and bond-end elements all aid in characterization, illuminating the chelation mode, stability, biochemistry, decomposition rate, and other features. Chemical properties are determined principally by structure; crystal structures are most revealing in this context<sup>[29]</sup>. The original diffraction data is collected as  $500\sim 600$  scatter plots, which are subjected to spatial analysis identifying the basic structural element which, however, does not correspond to the exact location of the core determinant. All elements must be analyzed, interpreted, marked, and finally, compared with objective values using dedicated software. If the deviations are small, the initial interpretation is realistic. Diluents and carriers interfere with single-crystal X-ray diffraction; pure crystalline material is required. Also, as the hydrogen atom contains only one electron, X-ray diffraction cannot identify hydrogen atoms in chelates. To accurately locate hydrogen atoms, electron or neutron diffraction is required.

### 2.5 TG-DSC analysis

Thermogravimetry (TG) determines the relationship between mass and temperature. Differential scanning calorimetry (DSC) measures the relationship between the power difference and temperature of a product and its substrates. In general, weight losses associated with chelation are derived from TG curves; the decomposition and melting point of the chelated material may be derived from DSC curves, yielding structural information. This method plays a very important role in determining the geometrical configurations of chelated molecules. In particular, the binding of water molecules in the chelate is revealed, as are the physicochemical properties of the sample under different temperature conditions<sup>[30-31]</sup>. Currently, most applications combine thermal weight analysis with DSC and infrared spectroscopy to qualitatively analyze chelates by reference to the relationship between thermal and structural properties<sup>[32]</sup>. The method should optimally be combined with other analyses. It is not appropriate to use this method alone when characterizing chelate structure; more background data and research are required.

### 2.6 Nuclear magnetic resonance

Nuclear magnetic resonance (NMR) is employed to explore chelate formation and its structural features using a high-intensity magnetic field to detect signal changes after absorption of electromagnetic radiation of various frequencies. NMR can be used to analyze the molecular structures of organic and inorganic compounds, especially chelates<sup>[33-34]</sup>. In practice, when determining the structure of a chelate compound, the chelating and chelated agents are often compared using NMR. Chelate formation is marked by the disappearance of some signal peaks, as well as changes in peak areas and positions. Chemical shifts in NMR spectra can also identify coordination status. NMR analyses, which focus on the structural characterization of peptide ligands. However, the use of NMR to evaluate chelates featuring amino acid and polysaccharide ligands has not been fully exploited.

To allow readers to quickly understand the various methods described above, we summarize their principles, advantages, and disadvantages in Table 2 below.

## 3 Discussion

Chemical fertilizers are the “food” of crops, but their effects on production levels worldwide are declining year by year. In China, for example, 1 kg of fertilizer afforded about 100 kg of output prior to the 1980s. In recent years, however, that output has fallen to 22 kg per 1 kg fertilizer, and it is declining at an average rate of  $1\text{ kg}\cdot\text{year}^{-1}$ . At the beginning of the 21<sup>st</sup> century, China recognized that the agricultural sector must achieve “zero growth of fertilizer use for principal crops” by 2020<sup>[35]</sup>. The Chinese fertilizer industry is thus

**Table 2 Comparison of methods used to characterize chelate structures**

Method	Principle	Advantage	Disadvantage
UV scanning analysis	The energy at the transition of the internal electron of the complex is different from the energy at the transition of the internal electron of the free ligand, so that the wavelength of the absorbed light is different.	The composition of the chelate can be determined for mononuclear, dimeric, multimeric and other states.	It is essential to use ligands that absorb light in the near-UV region, so higher requirements for the type of ligands
Fluorescence scanning analysis	The addition of metal ions shifts the maximum absorption peaks.	High sensitivity, fine selectivity, and wide linear range. Good performance in trace analysis.	This method is only applicable to chelates formed by different ligands with fluorescence excitation and emission spectroscopy. Often used as a supplementary means.
Infrared spectroscopy	Characterizing chelates based on comparison of chelating group status before and after complex formation.	Wide range of application, mature and high accuracy.	Requiring very pure ( $\geq 98\%$ ) crystalline samples. Heavy workload when analyzing unknown samples.
ESR	When using this technique, the electronic features of ligands must be first analyzed, followed by qualitative characterization of chelate coordination parameters.	Complex spectra can be simplified, and the peaks, identified. More straightforward.	Tedious operation. Higher requirements for the type of ligand substituents.
X-ray diffraction analysis	The crystal bond length, bond angle, and bond-end elements all aid in characterization, illuminating the chelation mode, stability, biochemistry, decomposition rate, and other features.	The result is more efficient to provide abundant molecular structure information. In the analysis of macromolecular space structure, the performance is outstanding.	Diluents and carriers interfere with single-crystal X-ray diffraction; pure crystalline material is required. Heavy workload.
TG-DSC	The effect of structural change on its physico-chemical properties at different temperatures is discussed in order to explore the chelate structure.	The geometry of the complex compounds can be determined.	Only as a means of supporting proof. The purity of the samples to will interfere with the analysis result.
NMR	Exploring chelate formation and its structural features using a high-intensity magnetic field to detect signal changes after absorption of electromagnetic radiation of various frequencies.	Effective in the detection of the chelate systems in which exist few useful contents and many kinds of similar substances.	High requirement for the type of chelates ligands. Need a non-zero spin and a magnetic moment.

tasked with the need to develop scientific and technological innovations culminating in new and efficient fertilizers. This would greatly reduce production costs and contamination. Chelated fertilizers have good rates of utilization and create minimal pollution. However, the development of such fertilizers faces certain problems and challenges if it is to become an important direction for future research and the application of fertilizer technology:

(1) The stability constants of chelated fertilizers are very important in terms of quality, optimizing production, fertilizer research, and marketing. Currently, no standard method

for calculation of stability constants has been accepted worldwide, compromising marketing, quality, and effective fertilizer use.

(2) Characterization of chelating fertilizers has improved greatly over the past 20 years, but amino acid chelates have received the most attention. Sugar alcohols are the first products of photosynthesis and would be better carriers of metals than are polyamino acids or humic acid. The structural features of compounds using sugar alcohols as chelates should be characterized and their mechanisms of action clarified to provide technical clues facilitating fertilizer improvements.

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## 螯合肥稳定性及结构表征研究

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**摘要** 近年来,随着农业集约化程度的不断提高,农业面源污染与农田土壤修复已成为农业研究中的重要内容,传统无机盐肥利用效率低下,“高效、环境友好型”的螯合肥研究与应用受到广泛关注。随着国际新形势下对土壤修复、农业面源污染减控等方面的重视,以及人们对高品质农产品需求的增加,螯合肥能否对此起到积极的促进作用,需要我们结合其稳定性、结构表征进行综合分析,从而为高端肥料市场的发展提供理论依据与数据支撑。螯合物稳定常数指螯合肥产品中已络合部分的稳定程度,我们可通过数学运算,如生成函数、来腾函数和福劳内乌斯函数等计算络(螯)合物的稳定常数。虽然迄今尚未建立统一的螯合肥稳定常数(或螯合强度)的测定标准方法,但国内外学者在这一领域做了大量的工作。但目前大多数测定方法尚不成熟,在稳定常数(或螯合强度)的定量参照数值的确定上也存在争议,且分析测定的螯合肥的方法以氨基酸螯合肥居多,对于非氨基酸螯合剂生成的螯合肥,需要进行综合评判以寻求测定各类配位体螯合物的标准方法。其次,结构决定性质,结构的表征有助于螯合肥的定性分析、实验现象的机理分析以及检测方法的选择。对于螯合物结构表征的方法,首先考虑的是螯合物单晶体或是纯品,但对于带有少量杂质的螯合物而言,数据可靠的结构表征手段往往无法快速构建。因此,在综合国内外相关研究的基础上,系统总结了螯合物稳定性测定与结构表征技术的研究,重点探讨各种技术手段的优缺点,提出螯合肥研究的发展方向,以期为螯合肥的科学开发与有效利用提供理论基础。

**关键词** 肥料; 稳定常数; 螯合强度; 结构表征

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