



# Quantitative measurement of metal chelation by fourier transform infrared spectroscopy



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## ABSTRACT

Nutritionally important minerals are more readily absorbed by living systems when complexed with organic acids, resulting in higher consumer demand and premium prices for these products. These chelated metals are produced by reaction of metal oxides and acids in aqueous solution. However, unreacted dry blends are sometimes misrepresented as metal chelates, when in reality they are only simple mixtures of the reactants typically used to synthesize them. This practice has increased interest in developing analytical methods that are capable of measuring the extent of metal chelation for quality control and regulatory compliance. We describe a novel method to rapidly measure the percent chelation of citric and malic acids with calcium, magnesium, and zinc. Utilization of attenuated total reflectance (FTIR-ATR) provides for the direct, rapid measurement of solid samples. The inclusion of an internal standard allows independent determination of either free or chelated acids from integrated areas in a single spectrum.

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## 1. Introduction

Nutritionally important minerals are more readily absorbed by living systems when they are combined with organic acids [1]. These combined metal-organic acid complexes are called chelated metals or mineral chelates and are more desirable than simple inorganic mineral oxides or carbonates to the nutritional and agriculture industries [2]. Chemical reactions used to synthesize mineral chelates are affected by a number of factors that can alter the extent of chelation in manufactured products. Quantitative analytical methods for determining the extent of chelation in solid samples are needed to support quality and regulatory testing [3–5], however, there are few rapid methods for measurement of the extent of chelation between metals and organic acids in their solid phases [6]. A wide variety of metal chelates have been studied by Fourier-transform infrared spectroscopy (FTIR). These include catechol-metal complexes [7,8], the adsorption of organic di-acids to minerals such as anatase and rutile [9] metal chelates in animal feeds [10] anhydrous

bivalent transition metal complexes [11], and mixtures of oxalate and malonate at water–goethite interfaces [12]. FTIR attenuated total reflectance (FTIR-ATR) methods for quantitative analysis of specific analytes in mixtures have been reported including mineral matter in coal [13], calcite to aragonite ratios in mollusk shells [14], chromium (*tris*) picolinate in pharmaceutical products [15], and lead binding to ethylenediaminetetraacetic acid (EDTA) [16]. Quantitative FTIR-ATR methods are enhanced by the addition of an internal standard in assays such as caffeine [17], vinyl acetate in poly(ethylene-co-vinyl acetate) [18], and surfactants in shampoo [19].

Free organic acids and their respective metal chelates exhibit significantly different FTIR absorption spectra, which have historically been used for qualitative identification of metal chelates. We studied these infrared spectral differences to see if they could be used to quantitatively determine the extent of chelation for calcium, magnesium, and zinc metal chelates with citric and malic acids in the solid state. These metals and organic acid combinations were chosen because they represent a significant market share of the mineral chelates currently sold into fertilizer and nutritional supplement markets. We also discovered that the inclusion of the internal standard, sodium dicyanamide, allowed the quantitative determination of both bound and free organic acids.

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## 2. Material and methods

### 2.1. Chemicals

Sodium dicyanamide (ACS, 96%), citric acid, and malic acid (ACS, 99 + %) were obtained from Aldrich–Sigma Chemical (St. Louis, MO). ACS-grade metal chelate standards (zinc malate, magnesium malate, calcium malate, zinc citrate, magnesium citrate, and calcium citrate) were obtained from Spectrum Chemical (New Brunswick, NJ).

### 2.2. Equipment and instrumentation

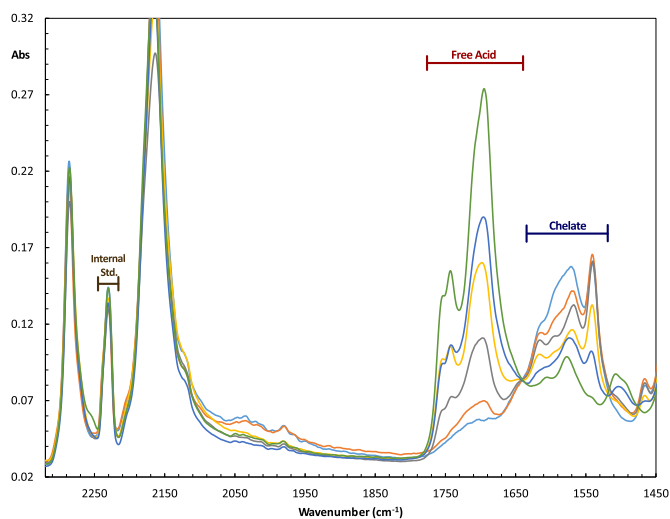
Homogeneity of the mixtures and finely ground powdered samples were attained using a ball grinder, Wig-L-Bug Model 30 (International Crystal Laboratories, Garfield, NJ). Infrared spectra were collected with a Thermo Nicolet 380 FTIR, equipped with Smart iTR Attenuated Total Reflectance (ATR) diamond Dia3525 crystal, 40 scans, with background correction between each sample. Thermo Scientific Omnic software (version 8.1) was used to collect and correct ATR spectra which were subsequently analyzed by the companion software, TQ Analyst (version 7.1.0.32), for peak area integrations.

### 2.3. Calibration

Pure solid standards were mixed in various ratios of metal chelates with their respective unreacted acids. Each of these calibration mixtures was then blended with an equal mass of the internal standard, sodium dicyanamide. Each mixture was then subjected to blending in a ball mill grinder for five minutes and stored under desiccation until scanned. Each analytical sample was mixed with an equal mass of internal standard, dried, and scanned in similar fashion to the calibration standards.

## 3. Results

Six sets of calibration data, one for each type of metal chelate, were collected and evaluated. Overlaid spectra for the calibration series of citric acid and calcium citrate mixtures is shown in Fig. 1.



**Fig. 1.** Overlaid FTIR-ATR spectra of calcium citrate/citric acid calibration mixtures, showing frequency ranges for integrated areas of the calcium citrate chelate, unchelated free citric acid, and internal standard.

The intensity of the calcium citrate absorbance between 1518 and 1637  $\text{cm}^{-1}$  increased with increasing concentration, while absorbance intensity for the free acid decreased with decreasing concentration in the same series of standards between 1637 and 1776  $\text{cm}^{-1}$  with an isosbestic point near 1637  $\text{cm}^{-1}$ . Sodium dicyanamide was chosen as an internal standard because of its unique absorption bands at 2100–2300  $\text{cm}^{-1}$ . Its well-defined peak at 2228  $\text{cm}^{-1}$  remained constant in all calibration standards and was unaffected by varying concentrations of chelated metals and free acids. The areas of the peaks in the regions of the spectrum corresponding to the free acid and metal chelate were individually determined by defining a baseline connecting the minima on each side of the respective region and subsequent integration. The spectral peak for the internal standard was integrated similarly. Resulting areas for each region of chelate and free acid were divided by the area of the internal standard to normalize spectral differences and allow independent determination of both free acid and metal chelate.

Fig. 2 shows the calibration plots of normalized area versus percent chelation for six different metal chelates. The negative-sloped calibration plots for each of the free acids clearly show the linear decrease of integrated areas with decreasing concentration. Conversely, calibration plots show a linear increase of each metal chelate with their increasing concentration.

This quantitative method was also utilized to successfully test a number of blind samples. Mixtures of free acids and their corresponding metal chelates were prepared and after mixing with internal standard were scanned and analyzed in the same fashion as the calibration standards. Using the appropriate calibration plots, normalized peak areas were used to calculate concentrations of both metal chelates and their unchelated free acids in the samples. Results are shown in Table 1.

## 4. Discussion

Our data indicates that FTIR-ATR spectra can be successfully applied to the quantitative measurement of chelation in solid metal chelates of malic and citric acids. Even though the spectral regions where these metal chelates and free acids absorb are broad compared to traditional single-peak absorptions, their integrated areas yield excellent results that are linear across the entire concentration range of 0–100%.

The ATR cell used in this study provides a relatively small path length across its surface (2 mm in diameter), giving rise to potential errors associated with path length differences. Ball-mill mixing was important in helping reduce standard deviations among replicates by increasing homogeneity of the mixture and decreasing particle size in each sample.

Water absorbs in the infra-red spectrum in the same region as these metal chelates. This potential source of error can be overcome by insuring that all samples and calibration standards are dry and stored under desiccation.

Generally, the simple comparison of two respective FTIR-ATR spectral intensities is insufficient for simultaneous quantitative measurement of each of the related analytes in a mixture. Dissimilar absorptivities of the two species must be taken into account when comparing peak areas to measure concentrations and non-absorbing components of the matrix can dilute analytes of interest. The inclusion of an internal standard helps minimize all these potential errors [17–19]. Sodium dicyanamide performed extremely well as an internal standard in our experiments. It stands alone in the IR spectrum with well-defined peaks that are free from interfering absorptions in the region of 2100–2300  $\text{cm}^{-1}$  and it does not react with any of the standards or samples tested in this study. A simple 1:1 addition of this internal standard to standards

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