



An Overview and Comparison of Methods for Cyanide Analysis

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Introduction

Cyanide analysis methods attempt to measure groups of compounds with similar chemical characteristics and report them as a single value. Various techniques are employed to separate specific types of cyanide complexes from each other and potential matrix interferences to achieve accurate quantitation (Figure 1).

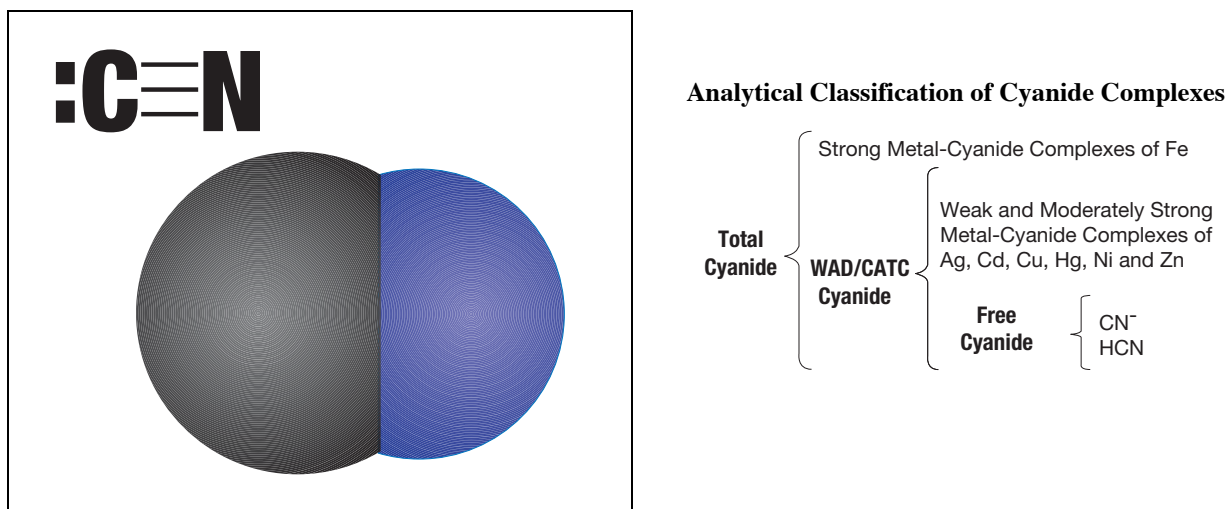


Figure 1. Cyanide refers to a monovalent anion consisting of carbon and nitrogen atoms with triple covalent bonds. Cyanide is very reactive and readily forms metal–cyanide complexes and organic compounds

The regulated community is presented with an array of conflicting definitions of cyanide species, which leads to misunderstandings about what the various techniques and methods actually measure. In fact, the U.S. EPA *Solutions to Analytical Chemistry Problems with Clean Water Act Methods* ⁽¹⁾, or “Pumpkin Guide”, states; “Next to oil and grease, cyanide is the pollutant for which the most matrix interferences have been reported to EPA.”

This study presents an overview and assessment of the most commonly used cyanide analysis methods including cyanide species measured, analytical techniques employed, potential matrix interferences, and final determinative steps.

Commonly Used Cyanide Analysis Methods

Free Cyanide

Free cyanide refers to the sum of hydrogen cyanide (HCN) and cyanide ion (CN⁻) in a sample ^(2, 3). Free cyanide is bioavailable and approximately a thousand times more toxic to aquatic organisms than it is to humans ⁽⁴⁾. Analytically, free cyanide is referred to as the amount of HCN liberated from solution at pH 6.0.

Weak to Moderately Strong Metal – Cyanide Complexes

Weak to moderately strong metal-cyanide complexes are compounds that dissociate and release hydrogen cyanide gas under mildly acidic conditions (pH 3 to 6). Cyanide species within this category include: simple cyanides—soluble/dissociable alkali metal and alkali earth metal-cyanide complexes (NaCN, KCN, Ca(CN)₂); weak metal-cyanide complexes (Zn(CN)₄²⁻, Cd(CN)₃⁻); and moderately strong metal-cyanide complexes (Cu(CN)₂⁻, Ni(CN)₄²⁻, Ag(CN)₂⁻) ^(2,3). Weak Acid Dissociable (WAD), Cyanide Amenable to Chlorination (CATC), and Ligand Exchange methods were developed to quantify the sum of these cyanide species as well as any free cyanide present in a sample.

Methods intended to measure weak to moderately strong metal–cyanide complexes also measure simple cyanides. Simple cyanides include free cyanide, alkali metal cyanides, alkali earth metal cyanides, and ammonium cyanide.

Strong Metal-Cyanide Complexes

Strong metal-cyanide complexes are compounds that require strongly acidic conditions (pH < 2) to dissociate and release hydrogen cyanide gas ⁽²⁾. Examples of strong metal-cyanide complexes include Fe(CN)₆²⁻, Fe(CN)₆⁴⁻, Co(CN)₆⁴⁻, and Au(CN)₂⁻. The strong acidic conditions used to dissociate these resistant metal-cyanide complexes readily dissociates all other cyanide species present in a sample. “Total Cyanide” is the term used in U.S. EPA methods to refer to the sum of all cyanide species that are converted to hydrogen cyanide following reflux distillation of a sample acid in a strong solution.

For a summary of cyanide analysis methods, refer to Table 1 .

Table 1: Summary of CN Analysis Methods

Description Name	Method	Description	Potential Interferences	Measurement
Free Cyanide	ASTM D 4282	Passive Diffusion at pH 6 and room temperature	<ul style="list-style-type: none"> Storage Measurement 	<ul style="list-style-type: none"> Manual chlorination of cyanide with chloramine-T and subsequent reaction with pyridine-barbituric acid. Maximum absorbance is determined by manual colorimetry.
	ASTM D 7237	Flow Injection Analysis (FIA) into a reagent at a pH of 6-8	<ul style="list-style-type: none"> Storage Measurement 	Gas Diffusion-Amperometry
Available Cyanide (CATC) (WAD)	SM 4500-CN G	<ul style="list-style-type: none"> Alkaline Chlorination to destroy all weak and dissociable metal-cyanide complexes and any free or simple cyanide. Two manual distillations (total-chlorinated)=CATC 	<ul style="list-style-type: none"> Excessive light, ammonia. Incomplete recovery on Ag-cyanide complexes. Storage Distillation Measurement 	<ul style="list-style-type: none"> Manual chlorination of cyanide with chloramine-T and subsequent reaction with pyridine-barbituric acid. Maximum absorbance is determined by manual colorimetry.
	ASTM D2036			
	ASTM D2036	Buffered (pH 4.5) manual distillation	<ul style="list-style-type: none"> Excess of Fe-cyanide complexes. Incomplete recovery on Hg-cyanide complexes. Storage Distillation Measurement 	<ul style="list-style-type: none"> Manual chlorination of cyanide with chloramine-T and subsequent reaction with pyridine-barbituric acid. Maximum absorbance is determined by manual colorimetry, Manual Ion Selective Electrode (ISE), Titration.
	ASTM D4374	Buffered (pH 4.5) automated flash distillation	<ul style="list-style-type: none"> Storage Distillation Measurement 	<ul style="list-style-type: none"> Automated chlorination of cyanide with chloramine-T and subsequent reaction with pyridine-barbituric acid. Automated colorimetry
	Kelada 01			
	OIA 1677	Pretreatment with ligand exchange reagents, room temperature automated gas diffusion.	<ul style="list-style-type: none"> Storage Measurement 	Amperometry
ASTM D6888				
Total Cyanide	SM 4500 CN D	<ul style="list-style-type: none"> Cyanide ion is released from cyanide complexes as HCN by means of macro manual reflux-distillation in the presence of a strong sulfuric acid solution and magnesium chloride. The HCN is swept into a dilute sodium hydroxide absorber solution. 	<ul style="list-style-type: none"> Storage Distillation Measurement Excessive Light 	Cyanide in the absorber solution is titrated with silver nitrate.
	SM 4500 CN E			<ul style="list-style-type: none"> Cyanide in the absorber solution is converted to cyanogen chloride by manual reaction with chloramine-T at pH <8. After reaction, the cyanogen chloride forms a red-blue color on addition of pyridine-barbituric acid reagent. Maximum color is determined by manual colorimetry.
	ASTM D2036	<ul style="list-style-type: none"> Cyanide ion is released from cyanide complexes as HCN by means of a macro, or scaled down manual reflux-distillation in the presence of a strong sulfuric acid solution and magnesium Chloride. The HCN is swept into a dilute sodium hydroxide absorber solution. 	<ul style="list-style-type: none"> Storage Distillation Measurement Excessive Light 	<ul style="list-style-type: none"> Cyanide in the absorber solution is titrated with silver nitrate. Cyanide in the absorber solution is determined manually by Ion Selective Electrode (ISE). Cyanide in the absorber solution is converted to cyanogen chloride by manual reaction with chloramine-T at pH <8. After reaction, the cyanogen chloride forms a red-blue color on addition of a pyridine-barbituric acid reagent. Maximum color is determined by manual colorimetry.
	EPA 335.4	<ul style="list-style-type: none"> Cyanide ion is released from cyanide complexes by means of a scaled down (midi) manual reflux-distillation in the presence of a strong sulfuric acid solution and magnesium chloride. The HCN is swept into a dilute sodium hydroxide absorber solution. 	<ul style="list-style-type: none"> Storage Distillation Measurement Excessive Light 	<ul style="list-style-type: none"> Cyanide in the absorber solution is converted to cyanogen chloride by automated reaction with chloramine-T at pH <8. After reaction the cyanogen chloride forms a red-blue color on addition of a pyridine-barbituric acid reagent. Maximum color is determined by automated colorimetry.
	Kelada 01, ASTM D4374, EPA 335.3	<ul style="list-style-type: none"> Cyanide ion is released from cyanide complexes by means of UV irradiation and automated flash distillation in the presence of a strong sulfuric acid solution. The HCN generated is injected into an auto chemistry analyzer chemistry cartridge. 	<ul style="list-style-type: none"> Storage UV Irradiation Distillation Measurement 	<ul style="list-style-type: none"> Cyanide in the adsorber solution is converted to cyanogen chloride by automated reaction with chloramine-T at pH <8. After reaction, the cyanogen forms a red-blue color on addition of a pyridine-barbituric acid reagent. Maximum color is determined by automated colorimetry.
	ASTM D7284	<ul style="list-style-type: none"> Cyanide ion is released from cyanide complexes by means of a scaled down (midi) manual reflux-distillation in the presence of a strong sulfuric acid solution and magnesium chloride. The HCN is swept into a dilute sodium hydroxide absorber solution. 	<ul style="list-style-type: none"> Storage Distillation Measurement 	Cyanide in the absorber solution is determined by automated gas diffusion amperometry.
	OIA 1678/ASTM D7511-09	<ul style="list-style-type: none"> Cyanide ion is released from cyanide complexes by UV irradiation. The HCN generated diffuses across a membrane and is measured amperometrically. 	<ul style="list-style-type: none"> Storage UV Irradiation Measurement 	Cyanide is determined by automated gas diffusion amperometry.

Potential Method Interferences

Sampling, Preservation, and Storage Interferences

Certain interferences occur during the sampling, preservation, and storage process and apply, to some extent, to all cyanide methods. Chemical preservatives added to samples to preserve the original concentration of cyanide in the sample need to be chosen according to the analytical method that will be used. In general, distillation methods are less forgiving and require extra care in sample pretreatment. Table 2 contains a summary of interferences that result from sample storage and preservation.

Sample Processing Interferences

The sample processing necessary to break metal-cyanide bonds and liberate the cyanide generated from the aqueous sample solution is not interference free. Often, in some sample matrices, the sample processing introduces so much doubt into the measurement that the results cannot be trusted at all. Table 2 contains a summary of interferences that can be introduced during sample processing.

Measurement Interferences

The final measurement technique used to determine the cyanide concentration is also not interference free. Since the final measurement is performed under the assumption that all interferences were previously removed, these interferences often go undetected. This is especially true for automated colorimetric methods. Table 2 contains a summary of interferences that may occur during the final cyanide measurement step.

Table 2: Summary of CN Method Interferences

Analysis Step	Compound	Process/Measurement Technique	Description of Interference
Sampling, Preservation, and Storage	Residual chlorine, peroxide, or other oxidizers	N/A	React with cyanide in solution rapidly decreasing the cyanide concentration. Oxidizers can co-exist with cyanide.
	Chloramines	N/A	React with sample at pH>10 increasing the cyanide concentration.
	Sulfide	N/A	Reacts with cyanide to form thiocyanate decreasing the cyanide concentration. Reaction is especially rapid if metal sulfides, such as lead sulfide, are present. The reaction is fairly slow without metal sulfides.
	Native Sulfur (colloidal sulfur)	N/A	Reacts with cyanide to form thiocyanate decreasing the cyanide concentration. Reaction is very fast with colloidal sulfur.
	Sulfite	N/A	Reacts with strong cyanide complexes at pH>10 decreasing the cyanide concentration. The reaction is almost immediate at pH>12.
	Light (<350 nm)	N/A	Reacts with strong metal-cyanide complexes releasing free cyanide.
	Ascorbic acid	N/A	Reacts with cyanide decreasing the cyanide concentration. Sample holding time when ascorbic acid is added is less than 48 hours. In some samples, ascorbic acid can react with ammonia or other nitrogen sources and increase the cyanide concentration.
	Formaldehyde	N/A	Reacts with cyanide decreasing the concentration. In some samples, formaldehyde reacts with ammonia or other nitrogen sources and increases the cyanide concentrations.
Sample Processing	Oxidizers	Distillation	Reacts with cyanide decreasing its concentration.
	Sulfide	Distillation	Distills into absorber solution and reacts with CN forming thiocyanate.
		Gas-diffusion	Passes through diffusion membrane.
	Sulfite (or Sulfur Dioxide)	Distillation	Reacts with cyanide decreasing its concentration. Distills into absorber solution and reacts with cyanide decreasing its concentration.
	Thiosulfate and other oxidized sulfur species (except sulfate)	Distillation	Decompose to form native sulfur and sulfur dioxide. React with cyanide decreasing its concentration. Sulfur Dioxide distills into absorber solution and reacts with cyanide decreasing its concentration.
	Thiocyanate	Cyanide Amenable to Chlorination (CATC)	Reacts with chlorine during alkaline chlorination and generates cyanide. Causes negative CATC results.
		Distillation	Decomposes to sulfur dioxide and reacts with cyanide decreasing its concentration. Sulfur dioxide distills into absorber solution.
		UV Irradiation	Can react at < 280 nm to form cyanide
	Thiocyanate + Nitrate or Nitrite	Distillation	Decompose to form cyanide
	Misc. Organics + Nitrate or Nitrite	Distillation	Decompose to form cyanide
Carbonate	Distillation	Excessive foaming and possible violent release of carbon dioxide	
	Gas diffusion	Passes through diffusion membrane	
Measurement	Sulfide	Titration	Detected as cyanide
		Ion Selective Electrode	Detected as cyanide
		Colorimetry	Detected as cyanide (at > 10–mg S/L)
		GD-Amperometry	Detected as cyanide (at > 50–mg S/L)
	Thiocyanate	Colorimetry	Detected as cyanide
	Fatty Acids	Titration	Mask end point
	Sulfur Dioxide	Colorimetry	Increase chloramine-T demand resulting in a negative bias. The increased demand many not be noticed with automated methods.
	Carbonates	GD-Amperometry	Negative bias at > 1,500–mg CO ₃ /L

Systematic Comparison of Method Interferences

While the underlying causes of cyanide analysis method interferences have been identified, no systematic approach has existed to help analysts assess the impact of those interferences, and select the best method for their intended application. Here, we describe a Cyanide Numerical Interference Rating System (CNIRS) that assigns numerical values to interferences and allows direct comparison of cyanide analysis methods. Under this system, the score increases each time a technique is cited for a known interference. The higher the CNIRS score, the greater the number of interferences reported for the technique (Table 3).

Interferences associated with sampling, preservation, and storage are assigned CNIRS scores based upon the degree of method automation. The rationale for this scoring is automated methods allow samples to be analyzed more quickly, which reduces interferences arising from preservation and storage.

Interferences associated with sample processing techniques (distillation, gas-diffusion, or UV-digestion) are assigned CNIRS scores based upon the number of times the particular technique is cited for a known cyanide interference in Table 2.

Interferences associated with measurement techniques (colorimetry or amperometry) are assigned CNIRS scores based upon the number of times the technique is cited for a known interference in Table 2.

Table 3: Cyanide Numerical Interference System (CNIRS) for Estimating Method Interferences

CN Technique	Score
Sampling, Preservation, and Storage ^(1,2)	
Automated Methods	1
Semi-Automated Method	2
Manual Method	3
Sample Processing	
Distillation	8
Gas-Diffusion	2
UV-irradiation	1
Measurement	
Colorimetry	3
GD-Amperometry	2

Tallying a composite CNIRS score for each cyanide analysis method allows the severity of method interferences to be classified and used for direct comparisons (Table 4). Using this approach, a method with a composite CNIRS score of 3 – 6 would fall in the Class I, low interference range. A method with a composite CNIRS score of 7 – 10 would be in the Class II, moderate interference range. Methods with composite CNIRS scores greater than ten (>10) would fall into Class III, high interference range.

The CNIRS scores of cyanide analysis methods are tabulated in Table 5 for direct comparison of interferences associated with each method and overall interference severity classifications. Figure 2 presents a graphic comparison of cyanide analysis methods based upon their respective composite CNIRS scores and interference classifications.

Table 4: Composite CNIRS Scoring Ranges for Classification of Cyanide Method Interferences

	Class I	Class II	Class II
Composite Interference Score	3–6	7–10	>10
Interference Severity Rating	Low	Moderate	High

Table 5: CNIRS Comparisons of Cyanide Method Interferences

Cyanide Species	Method	Storage	Processing	Measurement	CNIRS Total	Class
Free Cyanide	ASTM D4282	3	2	3	8	II
	ASTM D7237	1	2	2	5	I
Weak to Moderately Strong Metal–Cyanide Complexes	SM4500/ASTM D2036 (CATC)	3	8	3	14	III
	ASTM D2036	3	8	3	14	III
	ASTM D4734/Kelada 01	1	9	3	13	III
	ASTM D6888/OIA 1677	1	2	2	5	I
“Total” Cyanide	SM 4500	3	8	3	14	III
	ASTM D2036	3	8	3	14	III
	EPA 335.4	2	8	3	13	III
	ASTM D4734/Kelada 01/ EPA 335.3	1	9	3	13	III
	ASTM D7511–09/ OIA 1678	2	2	2	6	I
	ASTM D7284	2	8	2	12	III

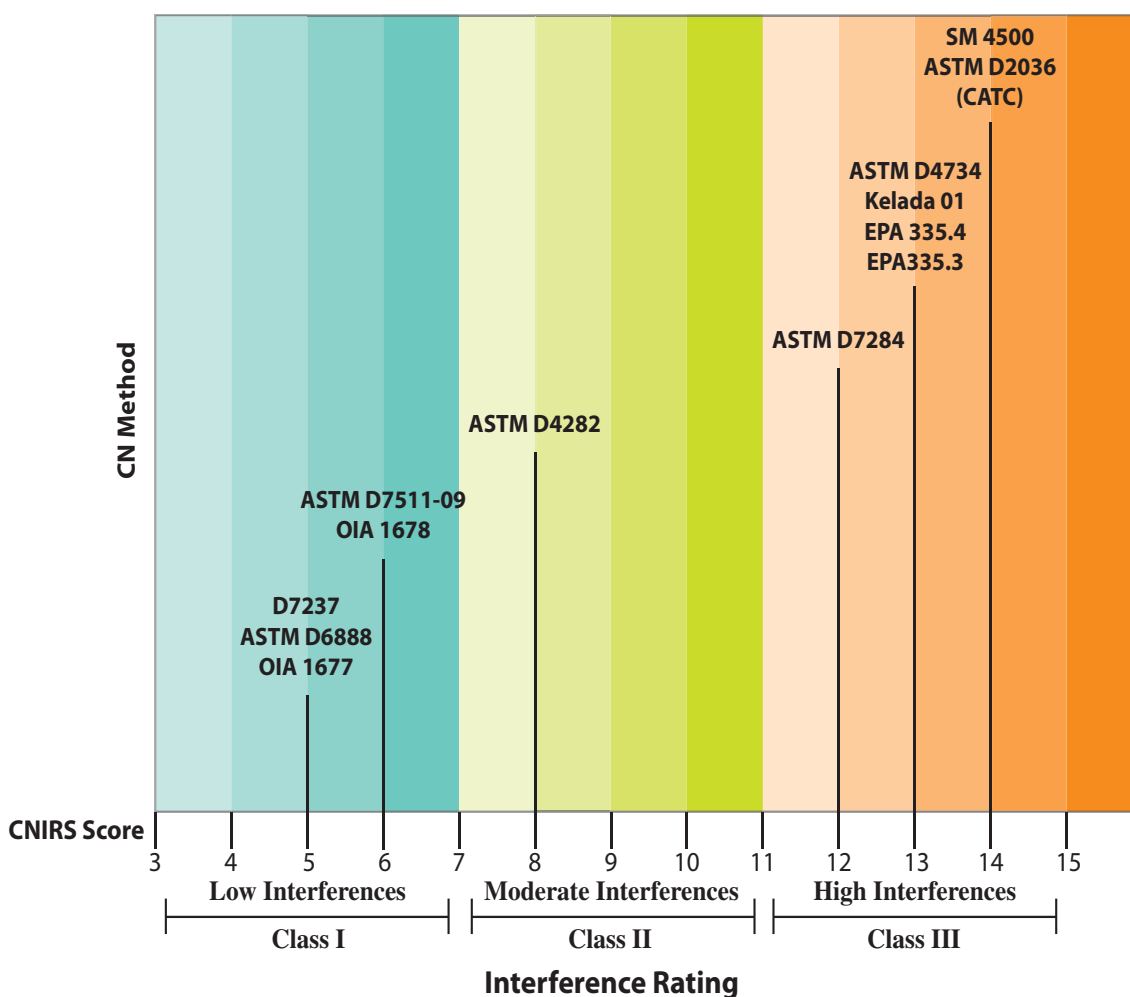


Figure 2. Cyanide Numerical Interference Rating System (CNIRS) Diagram

Summary & Conclusions

Environmental and public health regulations have driven the development of analytical methods for measuring cyanide species in diverse sample matrices. The interferences encountered in using these methods are largely dependent on the sample matrix and the sample processing prescribed in a particular method. While the underlying causes of cyanide analysis method interferences have been identified, a systematic approach to help analysts assess the impact of potential interferences and select the best method was unavailable.

A Cyanide Numerical Interference Rating System (CNIRS) that assigns numerical values to interferences and allows direct comparison of cyanide analysis methods has been described for the first time.

Composite CNIRS scores and interference severity ratings were tabulated for direct comparison of ASTM, USEPA, and Standard Methods cyanide analysis methods. Methods that employed distillation as a sample processing step and colorimetry for measurement were most interference prone. Methods that employed gas diffusion techniques and amperometry (GD-Amperometry) for measurement were less prone to interferences.

Cyanide analysis methods that can be performed with the OI Analytical CNSolution™ Cyanide Analyzer are shown in Table 6 along with their composite CNIRS scores. Class I methods are the least susceptible to interferences (gas-diffusion/amperometry methods) and are identified with a checkmark.

Table 6: Cyanide Methods Supported on the CNSolution™ Cyanide Analyzer

Cyanide Species	Method	Preparation	Measurement	CNIRS Score	Class I
Free	ASTM D7237	No Distillation	FIA GD-Amperometry	5	✓
CATC	ASTM D2036	Alkaline Chlorination, Double Distillation	Automated Colorimetry, or FIA GD-Amperometry	14	—
WAD		Buffered Distillation (pH 4.5)		14	—
Available	ASTM D6888, OIA 1677	No Distillation, Ligand Exchange	FIA GD-Amperometry	5	✓
Total	EPA 335.4	Manual Distillation	Semi-Automated Colorimetry	13	—
	ASTM D2036		Automated Colorimetry, or FIA GD-Amperometry	14	—
	ASTM D7284		FIA GD-Amperometry	12	—
	ASTM D7511-09, OIA 1678	UV Irradiation		6	✓

References

1. Solutions to Analytical Chemistry Problems with Clean Water Act Methods, USEPA Office of Science and Technology, March 2007
2. D 6696–05 Standard Guide for Understanding Cyanide Species, ASTM International, 2005
3. Cyanide Analysis Guide, OI Analytical Publication #2968
4. Cyanide Hazards to Fish, Wildlife and Invertebrates: A Synoptic Review, R. Eisler, U.S. Fish and Wildlife Service, Biological Report 85 (1.23), Dec. 1991



P.O. Box 9010
College Station, TX 77842-9010
Tel: (979) 690-1711 • Fax: (979) 690-0440 • www.oico.com