

AUTOMATED ANALYSIS OF EDIBLE OILS AND LUBRICANTS BY FTIR SPECTROSCOPY: PROBLEMS AND SOLUTIONS

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Presented at Laboratory Automation and Practices: An Overview
October 26, 2006, Albany NY

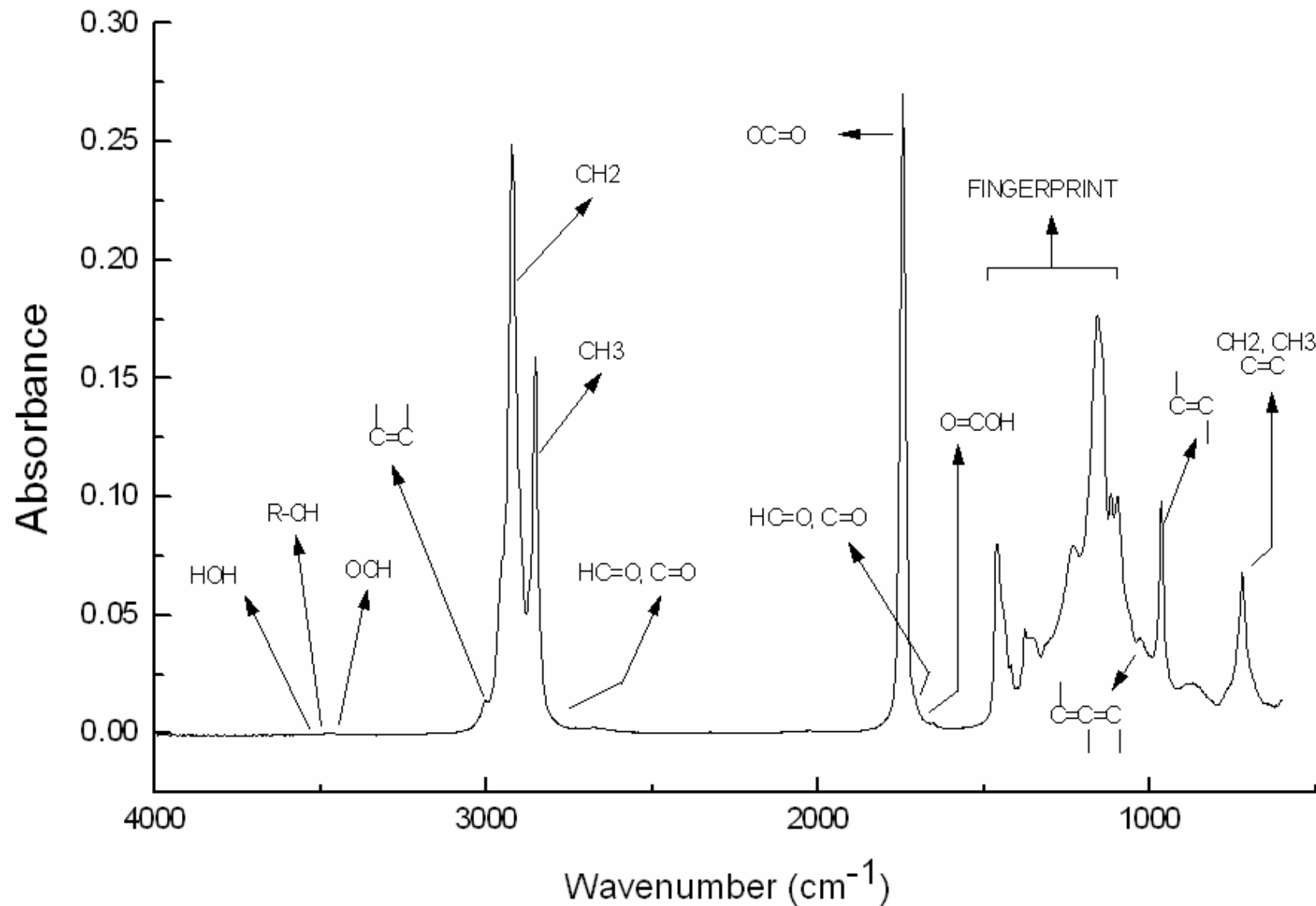
McGILL IR GROUP

- ◆ FOCUSES ON THE APPLICATION OF FTIR SPECTROSCOPY TO FOOD AND BIOLOGICAL MATRICES
- ◆ MY ROLE FOCUSES ON THE DEVELOPMENT OF RAPID INSTRUMENTAL METHODS FOR THE **QUANTITATIVE** ANALYSIS OF EDIBLE OILS AND LUBRICANTS BY FTIR SPECTROSCOPY
- ◆ CONCEPTUALLY THIS APPROACH IS BASED ON THE RICH FUNCTIONAL GROUP INFORMATION AVAILABLE IN THE MID-INFRARED PORTION OF THE SPECTRUM
- ◆ THE CHALLENGE HAS BEEN TO TAKE A TRADITIONALLY **QUALITATIVE** PROCEDURE QUANTITATIVE

FTIR SPECTROMETERS

- ◆ **MANY ADVANTAGES OVER TRADITIONAL DISPERSIVE INSTRUMENTS:**
 - COMPLETE SCAN IN 1 SECOND
 - MULTIPLE SCANS PROVIDE HIGH S/N RATIO BY SIGNAL AVERAGING
 - FOURIER TRANSFORM REQUIRES THAT THE COMPUTER BE AN INTEGRAL PART OF THE INSTRUMENT
 - REFERENCE LASER PROVIDES SUPERB WAVELENGTH ACCURACY ALLOWING FOR ACCURATE SPECTRAL DATA COLLECTION AND MANIPULATIONS
- ◆ **RESULT** – ENHANCED STABILITY AND UTILITY MAKING FTIR SPECTROSCOPY MORE AMENABLE TO DEVELOPMENT AS A **QUANTITATIVE TOOL**

MID-IR OIL SPECTRUM



IR OIL QUALITY INFORMATION

MEASURE	FUNCTIONAL GROUP(S)	CHEMICAL METHOD
DEGREE OF UNSATURATION	C=C	IODINE VALUE
TYPE OF UNSATURATION	<i>cis</i> -C=C, <i>trans</i> -C=C CH, C=C, C=C-C=C	TRANS ANALYSIS FATTY ACID PROFILE (GC)
CHAIN LENGTH	CH	SAPONIFICATION NUMBER
HYDROPEROXIDES	OOH	PEROXIDE VALUE
CARBONYL COMPOUNDS	HC=O	ANISIDINE VALUE
CARBOXYLIC ACIDS	COOH	FREE FATTY ACIDS
HYDROXYL GROUPS (MONO/DIGLYCERIDES)	OH	HYDROXYL NUMBER
MOISTURE	OH	MOISTURE CONTENT
SOLIDS CONTENT	CH, C=C, O-C=O	SOLID FAT INDEX

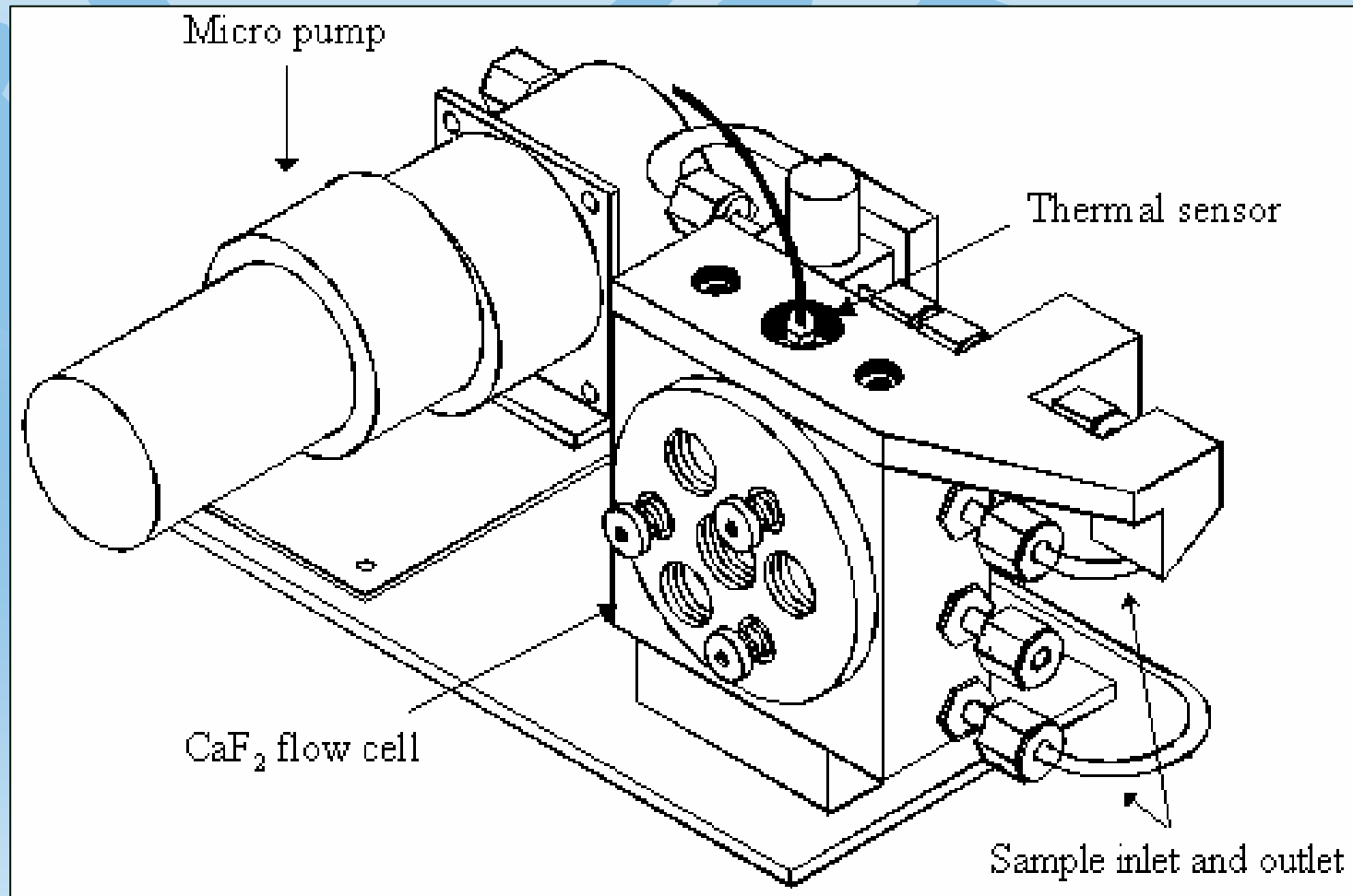
IMPLICATIONS AND CONSEQUENCES

- ◆ SPECTRUM CONTAINS INFORMATION RELATED TO MOST OIL QUALITY PARAMETERS USUALLY DETERMINED USING WET CHEMICAL METHODS
- ◆ HAVE DEVELOPED FTIR METHODS, ATTENDANT SOFTWARE AND IMPLEMENTED COMPLETE TURNKEY ANALYTICAL SYSTEMS
- ◆ A WIDE RANGE OF METHODS HAVE BEEN DEVELOPED, INCLUDING:
 - IV, TRANS, PV, SN, SFI AND H2O AS WELL AS SPINOFF LUBRICANT ANALYSES
- ◆ HAD TO OVERCOME MANY PROBLEMS

IMPEDIMENTS AND POTENTIAL SOLUTIONS

- ◆ IF QUANTITATIVE MID-IR ANALYSIS WERE EASY, PRACTICAL METHODOLOGIES WOULD HAVE BEEN DEVELOPED LONG AGO
- ◆ ALTHOUGH THERE ARE MANY DEVELOPMENTAL IMPEDIMENTS, THEY BOIL DOWN TO **SAMPLE HANDLING** AND **SPECTRAL INTERFERENCE** ISSUES
- ◆ SOLUTIONS INCLUDED THE DEVELOPMENT OF A CUSTOM SAMPLE HANDLING ACCESSORY AS WELL AS APPROPRIATE CALIBRATION APPROACHES IN RELATION TO THE ANALYSIS IN QUESTION

CUSTOM FLOW CELL



HEATED TRANSMISSION CELL - FACILITATES THE ANALYSIS OF VISCOUS OILS

CALIBRATION APPROACHES USED

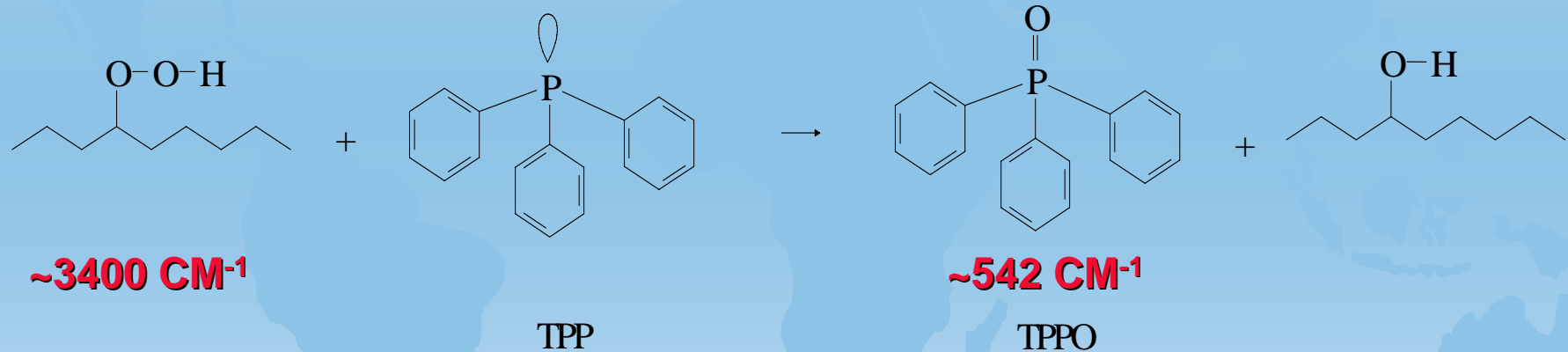
- ◆ SIGNAL TRANSDUCTION
 - ◆ MOLECULAR MODELS
 - ◆ PROCESS BASED
 - ◆ SUPPLEMENTARY CONCEPTS
 - SPECTRAL RECONSTITUTION (SR-FTIR)
 - 2D CORRELATION SPECTROSCOPY
- ☞ WILL BRIEFLY EXAMINE EXAMPLES OF EACH

(1) SIGNAL TRANSDUCTION

- ◆ USE A STOICHIOMETRIC REACTION TO CONVERT DIFFICULT TO MEASURE IR ABSORBING SPECIES INTO FTIR MEASURABLE PRODUCTS
- ◆ EXAMPLES:
 - PV ANALYSIS – HYDROPEROXIDES – LIPID OXIDATION
 - FFA ANALYSIS – HYDROLYSIS PRODUCTS OF TRIGLYCERIDES
- ◆ THE METHODS ARE UNIQUE IN THAT THEY REPRESENT **PRIMARY** METHODS AND USE SIMPLE PEAK HEIGHT QUANTITATION
- ◆ THEY DO NOT REQUIRE CALIBRATION AGAINST A “STANDARD” METHOD

SIGNAL TRANSDUCTION – PV ANALYSIS

- ◆ THIS METHOD IS BASED ON A STOICHIOMETRIC REACTION OF TRIPHENYLPHOSPHINE (TPP) WITH ROOH TO PRODUCE TRIPHENYLPHOSPHINE OXIDE (TPPO)



- ◆ TPPO FORMED IS DIRECTLY PROPORTIONAL TO ROOH AND PRODUCES A MUCH STRONGER IR SIGNAL

PV ANALYSIS PROTOCOL

- ◆ CALIBRATION IS DEVISED SIMPLY BY ADDING TPPO TO AN OIL
- ◆ ANALYSIS - WEIGH 30g OF OIL, ADD 10 DROPS OF A SATURATED TPP/HEXANOL SOLUTION
- ◆ SHAKE FOR 30 SEC AND MEASURE IN A 100 μm KCl TRANSMISSION CELL AT 542 cm^{-1} RELATIVE TO A BASELINE OF 550 cm^{-1}
 - ANALYSIS TAKES ~1 MIN
- ◆ THIS IS A *PRIMARY METHOD* AND IS SUBSTANTIALLY MORE REPRODUCIBLE THAN THE STANDARD AOCS TITRIMETRIC METHOD

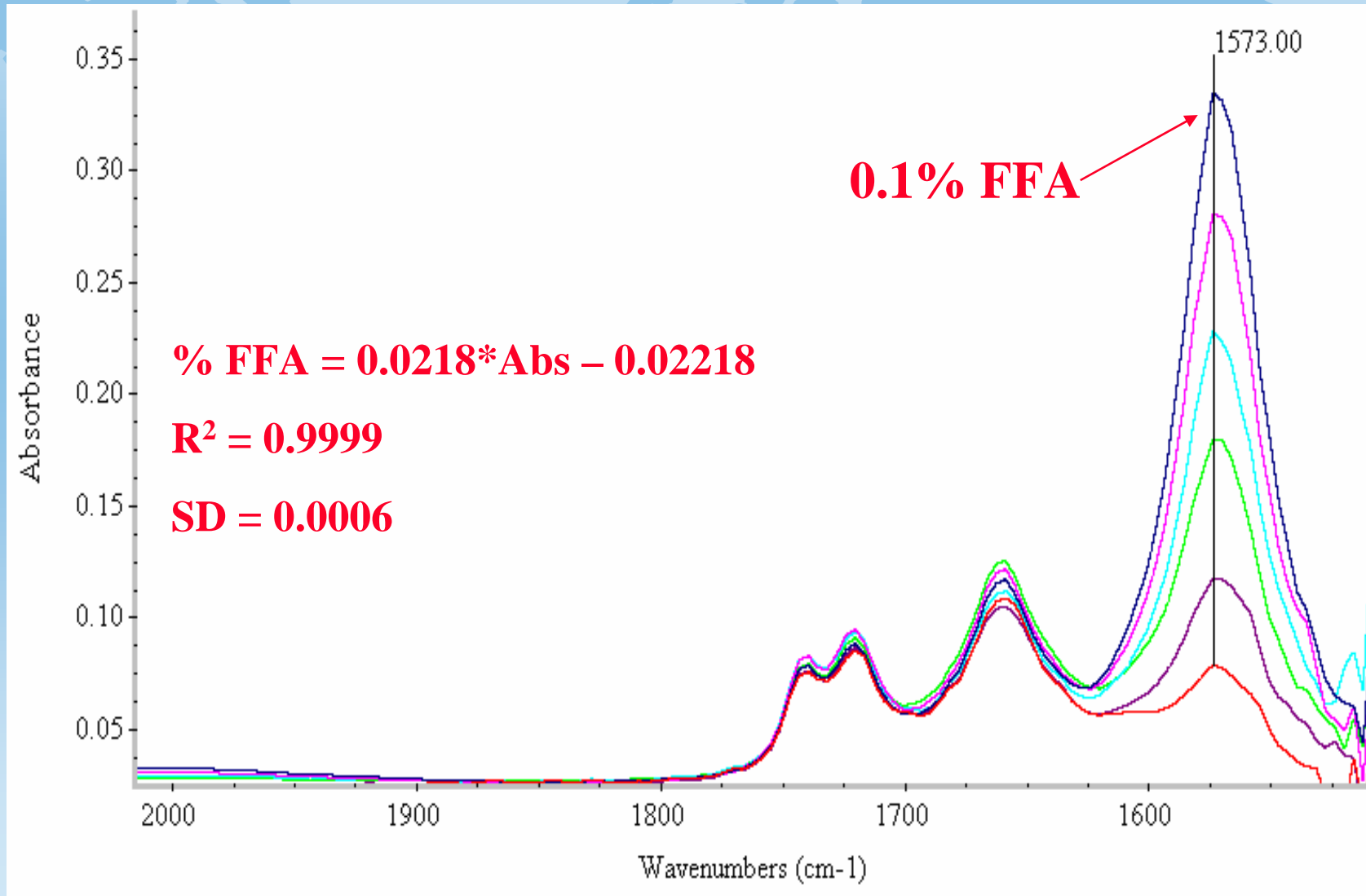
SIGNAL TRANSDUCTION – FFA ANALYSIS

- ◆ DEVELOPED A VERY SENSITIVE FFA METHOD FOR MONITORING LOW LEVELS OF FFAs IN REFINED OILS
- ◆ BASED ON THE SIMULTANEOUS EXTRACTION AND CONVERSION OF FFA INTO THEIR SALTS USING METHANOL CONTAINING SODIUM CARBODIIMIDE:



- ◆ OIL IS LEFT BEHIND AND **RCOO⁻** PROVIDES A CLEAR STRONG SPECTRAL SIGNAL WITHOUT ANY ATTENDANT SAPONIFICATION

CALIBRATION



A VERY SENSITIVE METHOD

- ◆ **CAN MEASURE FFA LEVELS AS LOW AS 0.001% - BY CONCENTRATING FFA, USING SIGNAL TRANSDUCTION AND USING DIFFERENTIAL SPECTROSCOPY**
- ◆ **AT THESE LEVELS OF SENSITIVITY, FFA ANALYSIS ALSO BECOMES A VEHICLE FOR MONITORING LIPID OXIDATION**
- ◆ **VERSATILE - CAN ALSO BE USED AS A ROUTINE FFA METHOD (0.1-4% FFA) SIMPLY BY CHANGING THE RATIO OF OIL TO METHANOL FROM 1:4 TO 5:1**
- ◆ **BECAUSE THE SAMPLE IS IN MEOH, IT CAN BE READILY RUN THROUGH A CONVENTIONAL FLOW CELL AND AUTOMATED**

(2) MOLECULAR MODEL APPROACH

- ◆ **THE USE PURE COMPOUNDS TO MODEL CONSTITUENTS OF INTEREST**
- ◆ **EXAMPLE - USE PURE TRIGLYCERIDES TO MODEL EDIBLE OILS (TRIACYLGLYCEROLS)**
- ◆ **AVOIDS NEED FOR REFERENCE ANALYSES SINCE CONSTITUENTS ARE MOLECULARLY DEFINED**
- ◆ **DEVELOPED AN GENERALIZED CIS/TRANS/IV/SN ANALYSIS PACKAGE USING PARTIAL LEAST SQUARES (PLS) BASED ON THIS CONCEPT**

MOLECULAR MODEL - TRANS ANALYSIS

- ◆ THE DIRECT ANALYSIS OF NEAT OIL PROVIDES MORE SENSITIVITY AND THE USE OF PLS OVERCOMES THE UNDERLYING ABSORPTION ERROR ASSOCIATED WITH TRANS ANALYSIS
- ◆ CAN BE USED FOR BOTH ATR AND TRANSMISSION BASED SAMPLE HANDLING SYSTEMS – BUT TRANSMISSION IS BETTER
- ◆ TRANSMISSION METHOD IS RAPID AND ACCURATE READILY MEASURING TO < 1% TRANS
- ◆ HAS BEEN VALIDATED AGAINST THE AOCS GC METHOD

(3) PROCESS BASED APPROACHES

- ◆ **CALIBRATION – USE PROCESS SAMPLES ANALYZED BY STANDARD METHODS, THE RESULTS OF WHICH ARE THEN RELATED TO SPECTRAL DATA USING PLS**
 - **EXAMPLES - AV, IV, SFI AND LIPID FATTY ACID COMPOSITION**
- ◆ **MORE COMPLEX UNDERTAKING - NEED TO ENSURE SAMPLES ARE REPRESENTATIVE**
- ◆ **NEED A RELIABLE REFERENCE METHOD –**
 - **CALIBRATION CAN ONLY BE AS GOOD AS THE REFERENCE METHOD**
- ◆ **NEED TO HAVE A GOOD UNDERSTANDING OF CHEMOMETRICS TO DEVELOP A ROBUST CALIBRATION AND VALIDATE IT EXTENSIVELY**

WELCOME TO ANOTHER WORLD...

- ◆ LUBRICANT ANALYSIS
 - VERY DIFFERENT, BUT WITH SOME COMONALITIES TO EDIBLE OILS
 - BOTH ARE IN THE DARK AGES ANALYTICALLY
- ◆ ONE OF THE FEW SECTORS WHERE FTIR ANALYSIS EXISTS IN AN AUTOMATED FORM
 - FTIR, AUTOSAMPLER, TRANSMISSION CELL AND PERISTALTIC PUMP
- ◆ FTIR IS USED FOR **SEMI-QUANTITATIVE** “*CONDITION MONITORING*” OF LUBRICANTS
 - MEASURES 7 COMPONENTS SIMULTANEOUSLY TO TRACK GENERAL CHANGES IN OIL QUALITY

CONDITION MONITORING

- ◆ METHODOLOGY IS KNOWN AS THE JOINT OIL ANALYSIS PROGRAM (JOAP) PROTOCOL – AN ASTM *PRACTICE*
- ◆ USED BY CENTRALIZED LABORATORIES TO MONITOR TRUCK FLEET, MILITARY VEHICLE, SHIP, PLANE AND MACHINERY LUBRICANTS
- ◆ USING BRUTE FORCE AND A SOLVENT WASH, COMMERCIAL FTIR SYSTEMS CAN HANDLE ~20 VISCOUS (OFTEN VERY SOOTY) LUBRICANT SAMPLES/H
- ◆ WE WERE ASKED TO BETTER

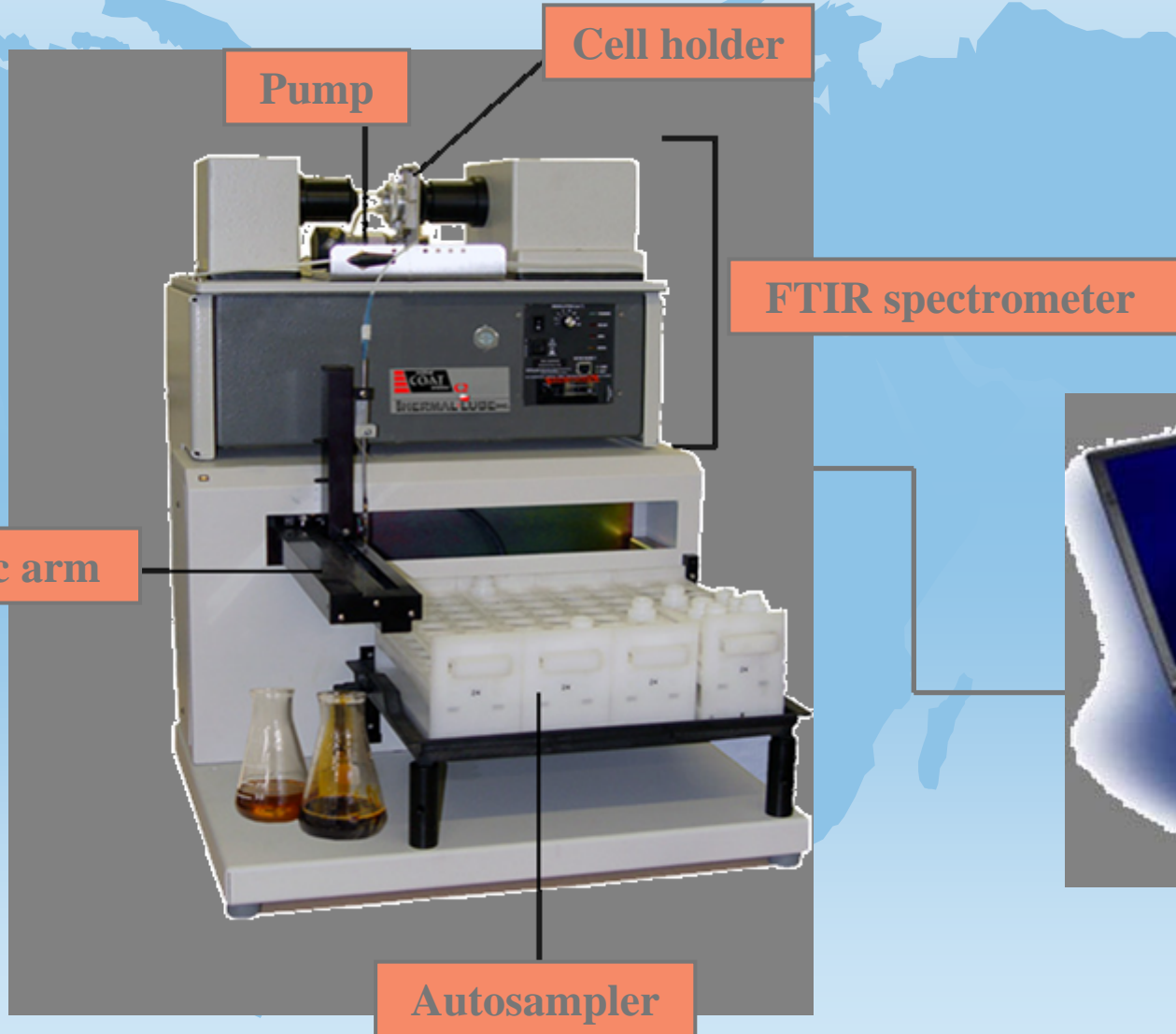
SPECTRAL RECONSTITUTION (SR-FTIR)

- ◆ OUR SOLUTION - DILUTE THE SAMPLE AND RECONSTITUTE THE SAMPLE SPECTRUM AFTER THE FACT – A PROCEDURE TERMED **SPECTRAL RECONSTITUTION (SR)**
- ◆ HOW? – DISOLVE A STRONG, UNIQUE SPECTRAL MARKER IN A CHEAP SOLVENT (OMS) AND USE THE MARKER'S UNIQUE ABSORPTION BAND TO QUANTITATE AND STRIP OUT THE SOLVENT SPECTRUM
- ◆ REASONED THAT IF **SR** MEASUREMENTS WERE REASONABLY ACCURATE, THE RESULTING FACIMILE SPECTRUM SHOULD CORRELATE WELL WITH THAT OF THE ORIGINAL NEAT OIL SPECTRUM

SR-FTIR RESULT

- ◆ SPECTRAL RECONSTITUTION WORKED EXTREMELY WELL WITH SPECTRAL CORRESPONDANCE EFFECTIVELY 1:1
- ◆ AN AUTOMATED FTIR SYSTEM WAS DESIGNED CAPABLE OF RUNNING THE JOAP PROTOCOL @ 120 SAMPLES/H
- ◆ SR-FTIR ELIMINATED SOLVENT WASHES, CELL CLOGGING, AND WEAR PROBLEMS
- ◆ THIS FTIR SYSTEM IS ALSO USED FOR NEW **QUANTITATIVE** AN, BN AND H₂O METHODS DEVELOPED SPECIFICALLY FOR LUBRICANTS

INSTRUMENTATION



IS SR-FTIR QUANTITATIVE?

- ◆ YES – DEMONSTRATED THAT SR-FTIR *TRANS* ANALYSIS WAS NOT ONLY QUANTITATIVE, BUT ALSO ~20x MORE SENSITIVE THAN SB-ATR
- ◆ SR-FTIR APPROACH FACILITATES AUTOMATION
 - NO SPECIAL ACCESSORIES
 - EASY TO LOAD AND AUTOMATE
 - DEVELOPED THE SOFTWARE THAT DOES ALL THE WORK
- ◆ *TRANS* QUANTITATION BODES WELL FOR CONVERSION OF EARLIER IR METHODS DEVELOPED FOR NEAT OILS

2D FIX FOR AN OLD PROBLEM

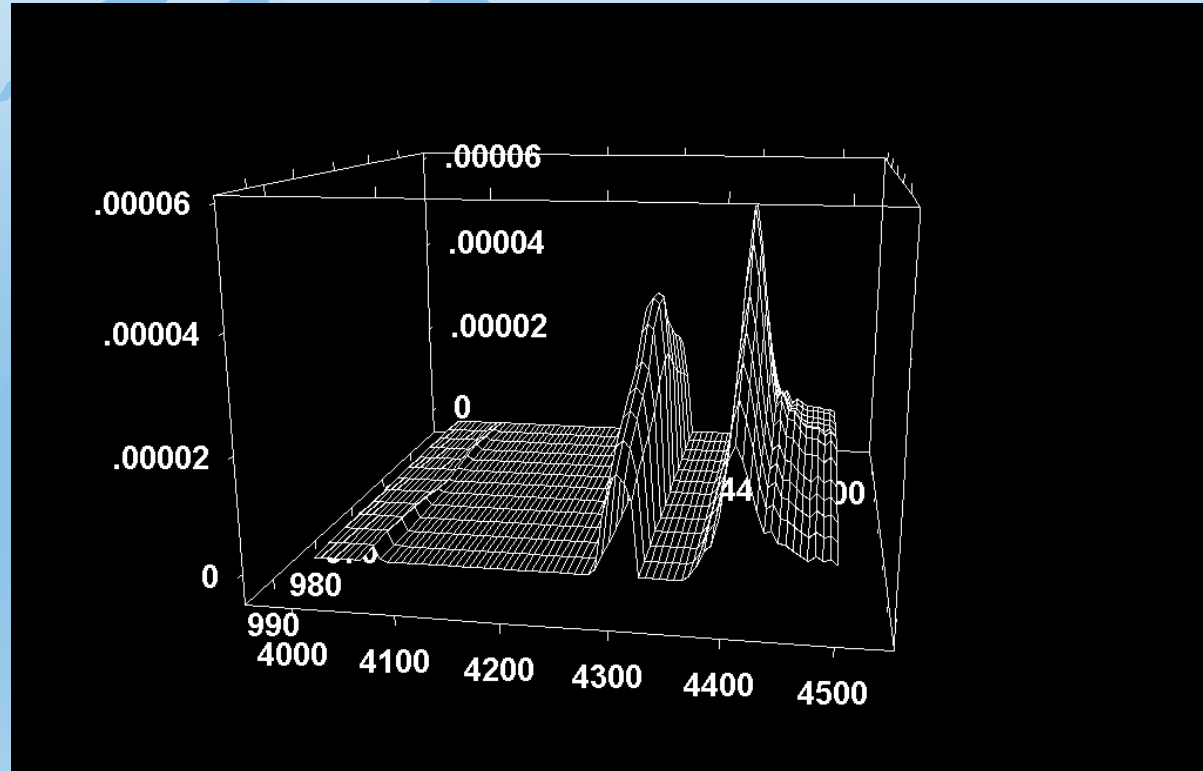
TRANS UNDERLYING ABSORPTIONS

- ◆ CONVENTIONAL FTIR RATIO METHOD REQUIRES A *TRANS*-FREE REFERENCE OIL
 - LIMITS METHOD TO OILS OF KNOWN PROVENANCE
 - MUST HAVE A *TRANS*-FREE VERSION ON HAND
 - ↳ AN UNREALISTIC REQUIREMENT FOR A GENERAL ANALYTICAL METHOD
- ◆ USING 2D CORRELATION SPECTROSCOPY IN CONJUNCTION WITH SR-FTIR
 - HAVE FOUND ALTERNATE SPECTRAL REGIONS WHICH CORRELATE WELL WITH UNDERLYING *TRANS* ABSORPTIONS

2D FIX FOR TRANS ANALYSIS

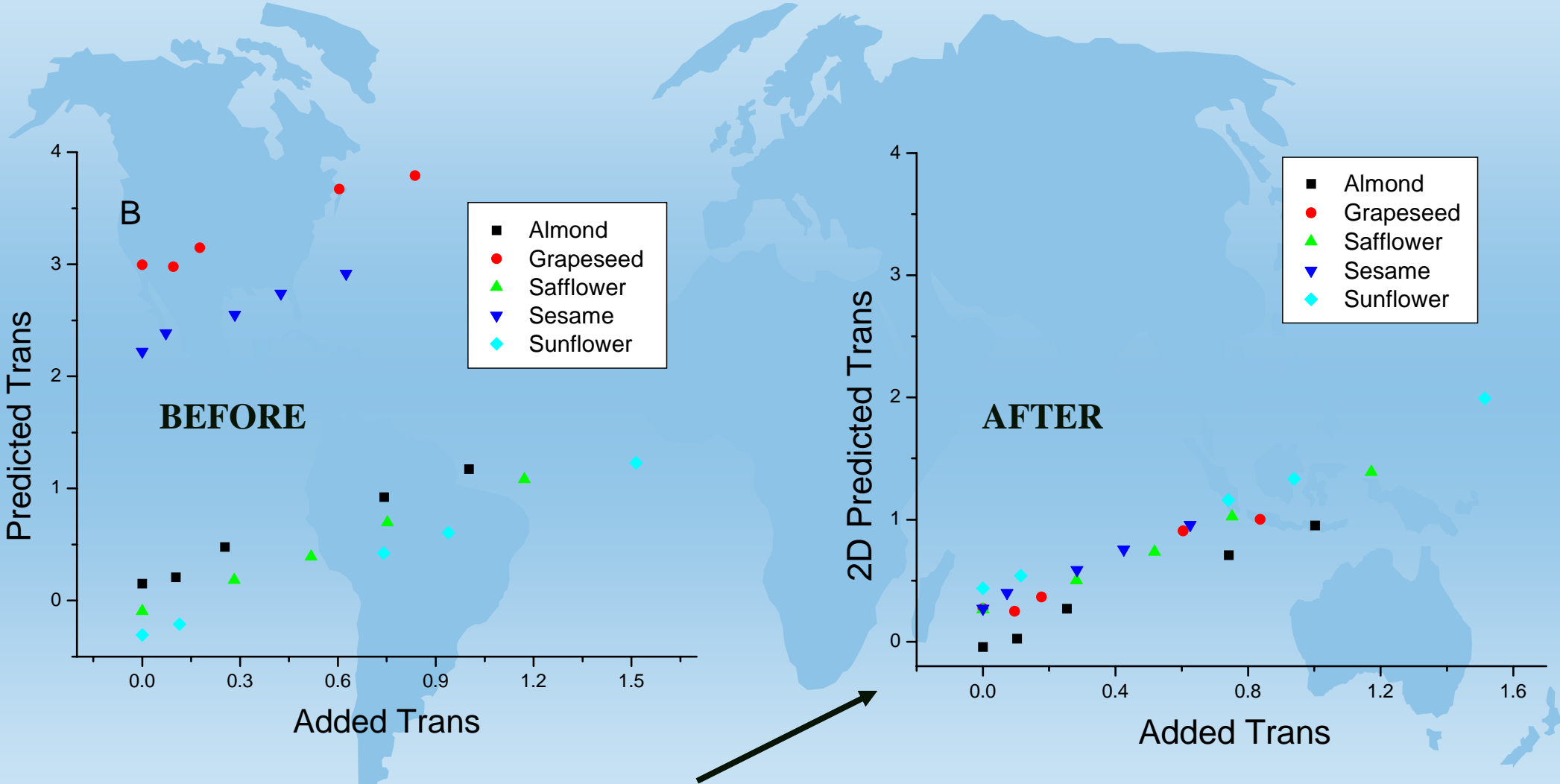
◆ 2D CORRELATION MAP OF SPECTRAL REGIONS RELATED TO 945-990 CM^{-1}

◆ THESE ALTERNATE WAVELENGTHS PROVIDE ACCURATE ESTIMATES FOR UNDERLYING ABSORPTIONS, ELIMINATING THE NEED FOR A REFERENCE OIL



◆ SUCCESS WILL MAKE FTIR A PRACTICAL ALTERNATIVE TO GC FOR *TRANS* DETERMINATION IN EDIBLE OILS

BEFORE AND AFTER 2D CORRECTION



$2DTrans = 0.19 + 1.02(Added\ Trans)$ $SD = 0.10$ $R = 0.97$

PUTTING IT ALL IN PERSPECTIVE

- ◆ **PRINCIPLES OF FTIR QUANTITATIVE ANALYSIS FOR EDIBLE OILS ARE NOW WELL ESTABLISHED**
- ◆ **HAVE TRANSFERRED THEM TO LUBRICANTS AND VICE VERSA – BRINGING IN SR-FTIR**
- ◆ **FTIR METHODOLOGY MOVING FROM THE RESEARCH LAB INTO THE QC WORLD WHERE IT HAS A PLACE**
 - **CAN NOW REPLACE KEY TEDIOUS, AND ENVIRONMENTALLY PROBLEMATIC WET CHEMICAL METHODS WITH MORE RAPID INSTRUMENTAL METHODS**

CONCLUSION

- ◆ **SR-FTIR IS LIKELY A KEY STEP FORWARD**
 - CAN LIKELY OVERCOME TRANSMISSION CELL SAMPLE HANDLING LIMITATIONS ASSOCIATED WITH ALL TYPES OF VISCOUS SAMPLES, NOT ONLY EDIBLE OILS
- ◆ **OPENS A NEW DOOR – I SEE FTIR PROVIDING RAPID LIPID NUTRITIONAL DATA (TRANS, SATURATED, MONO, POLY FAT) AND EVEN FATTY ACID COMPOSITION IN LIEU OF GC**
- ◆ **SEE FUTURE CONVERSION OF FTIR METHODS TO SR-FTIR PROTOCOLS TO FUTURE FACILITATE AUTOMATION**

THANK YOU



ADDITIONAL INFORMATION:

<http://www.agrenv.mcgill.ca/foodscience/irg2.htm>

<http://www.scriptshifter.com/thermal-lube/english/index.html>