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Nuclear Magnetic Resonance (NMR) Handbook

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United States Department of Agriculture
Agricultural Marketing Service
Federal Grain Inspection Service

Program Handbook

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Nuclear Magnetic Resonance Testing for Sunflower Seed Oil

Foreword

The Nuclear Magnetic Resonance (NMR) Handbook was established to provide official personnel with procedures to follow for the testing and certification of sunflower seed oil using the NMR method. All official inspection personnel authorized or licensed to perform NMR testing must reference this handbook for procedures.

This handbook was revised and reformatted to incorporate FGIS's move to AMS, minor process changes, updated forms, inclusion of FGIS PN 14-04 Approval of New Nuclear Magnetic Resonance (NMR) Instruments (11/21/2013) as well as general revisions and formatting. In addition, definitions, tables, and processes were updated to the current standards. The specific updates are listed in chapter 8 of this handbook.

The mention of firm names or trade products does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over other firms or similar products not mentioned. Except for the NMR instrument, equivalent equipment may be used in place of the items listed.

This handbook supersedes the FGIS Nuclear Magnetic Resonance (NMR) Handbook dated October 1, 2009.

Distribution: FGIS, OSP, Industry

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TABLE OF CONTENTS

CHAPTER 1
INTRODUCTION

Contents

1.1 SCOPE

Testing sunflower seed for oil content as "official criteria" is authorized under Section 7(b) of the United States Grain Standards Act (USGSA), as amended. All official sunflower seed oil analysis under the USGSA is performed in accordance with procedures prescribed in this handbook by authorized Federal Grain Inspection Service (FGIS) employees or licensed personnel employed by delegated/designated agencies.

The pulsed low resolution Nuclear Magnetic Resonance (NMR) instruments are the only approved instruments for official sunflower seed oil determination. The NMR method is based on the principle of activating hydrogen atoms in the oil using electromagnetic radiation and a magnet. The NMR reading is a measure of the number of activated hydrogen atoms. The FGIS-Technology and Science Division (TSD) will use the petroleum ether oil extraction method (AOCS method number Ai 3-75) as the reference method to which the NMR instruments are calibrated and referenced.

Field instruments are aligned to the reference method through the Sunflower Seed Standard (SSS) samples provided by TSD. These SSS samples are assigned NMR oil determinations based on multiple analyses of the SSS on the master NMR instruments maintained at TSD. The master NMR instruments are aligned to the reference method using a set of sunflower seed samples with known reference oil values prior to assigning the NMR oil determination values to the SSS.

This handbook establishes procedures for officially determining and certificating oil content of sunflower seed, monitoring the accuracy of official sunflower seed oil results, and maintaining sunflower seed oil equipment accuracy.

1.2 DEFINITIONS

Calibration - An alignment of the instrument signal with the established oil concentration using a calibration curve. The calibration curve is defined by the slope, intercept, and correlation coefficient.

Calibration Verification - A verification of the calibration curve by analyzing the sunflower seed standard prior to sample analysis.

Check Samples - Sunflower seed samples tested by TSD and distributed to all specified service points for monitoring the uniformity of field results.

Collaborative Study - A study designed to compare NMR oil values determined by different laboratories.

Constituent - Compounds for which an analysis is made in a product (i.e., oil in sunflower seed.)

Correlation - The interdependency of one variable on another (i.e., the amount of oil extractable from a sample using petroleum ether and NMR response.)

Correlation Coefficient – A numerical measure of some type of correlation (e.g., the relationship of two variables on each other such as instrument signal and oil concentration). It is the value recorded during an instrument calibration (CC or R^2). The correlation coefficient must be greater than 0.9900.

Daily Checks - Validation routine that verifies that the instrument hardware and signal intensity is operating within the manufacturer parameters.

Intercept - The offset value needed for the slope of a calibration curve to reach zero. This value is recorded during an instrument calibration.

Monitor File Samples - Sunflower seed samples randomly selected from the market, which are analyzed and compared to a monitoring office. NMR portion are subsamples taken from the Monitor File Sample.

NMR Portion - Sunflower seed portion that is analyzed on NMR instrumentation and used to compare instrument performance between monitoring offices.

NMR Response - A measure of the number of activated hydrogen atoms within a magnetic field.

Oil - A mixture of a glyceride ester of fatty acids widely occurring in organic tissues that are liquid at room temperature.

Petroleum Ether Oil Extraction - A chemical determination of percent oil in a sample.

Pulsed NMR - A technique used for determining the oil content of a sunflower seed sample by measuring the number of electromagnetically activated hydrogen atoms present in liquid oil. Pulsed NMR instruments apply external radio frequency energy to samples as short pulses lasting a few microseconds. The pulses simultaneously excite all of the nuclei in a sample and the signal (called a free induction decay) is measured after the pulse. All modern NMR instruments use pulsed techniques.

Reference Value - An oil value determined by TSD for each of the Sunflower Seed Standard and sunflower seed check samples.

Slope - The degree of slant of the regression line of a calibration curve.

Specified Service Point (SSP) - A city, town, or other location specified by an agency for the performance of official inspection or Class X or Class Y weighing services and within which the agency or one or more of its inspectors or weighers is located.

Sunflower Seed - Also known as cultivated sunflower seed, which is sunflower seed grown for oil content.

Sunflower Seed Standard (SSS) - Dried and sealed sunflower seed samples with established weights and NMR oil values. SSS are prepared by TSD and distributed to the SSP to calibrate NMR instruments.

Tuning Sample (TS) - A sample provided by the NMR manufacturer that gives a signal large enough to tune the NMR instrument. Used to perform the daily check of an instrument. May also be referred to as a daily check sample or autotune sample.

1.3 RESPONSIBILITIES

The general responsibilities for the sunflower seed oil testing program are as follows:

a. Responsibilities of the Technology and Science Division.

(1) Maintain the standard reference petroleum ether oil extraction laboratory for FGIS and create calibrations for approved NMR instruments used for official NMR oil testing.

(2) Establish the official oil content of all SSS.

(3) Provide SSS samples to field offices and all SSP providing official NMR sunflower seed oil determination.

(4) Monitor the capability of the official sunflower seed oil testing program.

(5) When necessary, review sunflower seed oil analysis procedures at SSP locations.

(6) Recommend corrective and follow-up action when problems are detected.

(7) Provide technical support and training to official personnel in matters relating to oil analysis.

(8) Initiate and/or conduct and report collaborative and/or special studies as needed.

(9) When needed, perform calibration studies and make recommendations.

(10) Provide Board appeal inspection, and where applicable, appeal inspection for sunflower seed oil testing.

(11) Issue certificates and assess fees for Board appeal, and where applicable, appeal inspection service.

(12) Where applicable, coordinate and maintain the sunflower seed NMR oil testing program within the circuit.

b. Responsibilities of Domestic Inspection Operation Office (DIOO):

(1) Immediately inform TSD of problems detected in the circuit.

(2) Assist TSD in conducting collaborative and/or special studies.

c. Responsibilities of Official Agency Managers/State Cooperators.

(1) Official service providers must observe certain guidelines when establishing new testing laboratories and/or placing new equipment in service.

(2) Coordinate and maintain a sunflower seed oil testing program within the assigned geographic area.

(3) Perform original and reinspection NMR sunflower seed oil testing services within the assigned geographic area and forward file samples for appeal sunflower seed oil testing services to TSD.

(4) Select and forward samples for monitoring to TSD.

(5) Routinely review oil analysis procedures at SSP within the assigned geographic area.

(6) Permit only official personnel who are trained and licensed for sunflower seed oil testing to perform such activities.

(7) Provide technical support and training to licensed inspection personnel within the assigned geographic area.

(8) Assist TSD in conducting collaborative and/or special studies.

(9) Inform the monitoring field office manager and/or TSD, as applicable, of problems detected within the assigned geographic area and initiate corrective and follow-up action.

1.4 DISCLAIMER CLAUSE

The mention of firm names or trade products does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over other firms or similar products not mentioned.

CHAPTER 2
NMR OIL TESTING EQUIPMENT

Contents

2.1 PURPOSE

To ensure that the FGIS sunflower oil program is applied uniformly by all SSP, that only approved pulsed NMR equipment and procedures are used, that equipment maintenance and testing schedules are followed, and that laboratory setups conform to FGIS specifications.

2.2 APPROVED EQUIPMENT

The following equipment is approved for official NMR sunflower oil determinations.

Aluminum Dishes - Aluminum dishes with lids, approximately 90 millimeters (mm) in diameter and 50 mm deep with closely fitted slip-on cover.

Balance - An approved electronic balance with 0.01gram precision and capability of connecting to a computer or NMR instrument using a RS-232 or equivalent output port.

Bottle Brushes - Bottle brushes for cleaning NMR sample tubes.

Desiccating Cabinet - An airtight cabinet which can be equipped with a desiccant material to maintain a very low relative humidity environment.

Desiccant - Silica gel for drying, indicating, 6-16 mesh.

Electronic Power Conditioner (Optional) - An electronic power line conditioner (Sola model No. EPC 150-60, Tripp Lite model LS-604 or equivalent).

Forced Air Convection Oven - A forced air convection oven (Blue M Model OV-490A- 2 or equivalent).

NMR Instruments

a. Oxford Instruments America, Inc. pulsed NMR MQC-5 equipped with 5 Mega Hertz (MHz) magnet and 150 milliliters (ml) magnet coil assembly. (Oxford Instruments Inc., 300 Baker Avenue, Suite 150, Concord, MA 01742, phone 1-800-447-4717).

b. Bruker Minispec mq7.5 pulsed NMR equipped with 7.5 MHz magnet and 150 ml magnet coil assembly. (Bruker Canada Ltd., Milton, Ontario L9T 1Y6, Canada, phone 1-905-876-4641).

c. Bruker pulsed NMR model Minispec MQ-One Seed Analyzer XL equipped with 7.5 MHz magnet and 150 ml magnet coil assembly. (Bruker Canada Ltd., Milton, Ontario L9T 1Y6, Canada, phone 1-905-876-4641).

NMR Sample Tubes - NMR sample tubes for 150-ml NMR magnet coil assembly. Typically, 50-mm glass tubes with high and low depth markings.

Rubber Stoppers - Rubber stopper for NMR sample tube, size No. 10.

Thermometers - Thermometer with 1° to 51°C scale and 0.1°C divisions.

2.3 OIL TESTING FACILITIES

Equipment location and environmental factors can affect the performance of NMR sunflower seed oil testing equipment. The space and facilities used by official personnel must meet the specifications outlined below.

a. Location of Equipment.

CAUTION: Do not place the NMR instrument on a steel table.

The method used for determining the oil content of sunflower seed samples utilizes a magnet with predetermined electromagnetic strength to activate the hydrogen atoms present in the sample. Metal objects or a strong magnet placed near the NMR equipment may interfere with the electromagnetic field and produce erroneous results. Therefore, do not place metal objects adjacent to the NMR equipment.

A vibration-free table should be used to support equipment. Also, when more than one electronic instrument is located in the same work area, maintain at least 60 centimeters (approximately 2 feet) distance between instruments.

In addition, NMR equipment must be placed in a location conducive to a stable environment and shielded from electrical or electromagnetic interferences. NMR equipment must be protected from drafts, heating and cooling vents or devices, and preferably be kept away from outside walls and windows.

b. Temperature.

Maintain a constant temperature between 18°C (65°F) and 30°C (85°F) in the room where the NMR instrument is located. Record room temperature using a calibrated thermometer located near the NMR instrument.

Insert the thermometer into a small glass or plastic bottle filled with sunflower seed to reduce erroneous readings. The depth of the sunflower seed must be sufficient to cover the insertion level of the thermometer.

Fluctuation in room or sample temperature adversely affects analysis results. After calibration, a change in room or sample temperature greater than ± 1.0°C will require re-calibration using the SSS. Therefore, locate the NMR equipment in a room where the temperature remains very stable to minimize the need for re-calibration.

c. Power Supply.

The power for NMR instruments shall be supplied by a 120 ±10 VAC 15-20 amp

dedicated circuit. A maximum of two electronic instruments and associated printers may be placed on one dedicated circuit (2 NMR or 1 NMR and 1 Near Infrared Transmittance (NIRT) instrument). To reduce interference from other sources, do not place other equipment on the circuit.

d. Dust.

CAUTION: Do not use compressed air for clean-up purposes because propellant residue may contaminate area.

Accessible surfaces of the NMR instrument, balance, and surrounding area shall be maintained essentially free from contaminants. Use a vacuum cleaner and brush for maintaining a clean and dust-free environment in the sunflower seed testing area.

At locations where a dust collection system is not available, place the NMR instrument and balance in a room separate from all dust-producing equipment such as grinders, dockage testers, and dividers.

2.4 INITIAL LABORATORY SETUP

Official service providers must observe certain guidelines when establishing new testing laboratories and/or placing new equipment in service.

a. New Laboratories.

Upon request, TSD will assist agencies in planning and preparing laboratories for official oil testing service. Agency managers must notify the field office manager, where applicable, or TSD that a new laboratory is being planned and provide a diagram of the proposed laboratory design. The diagram should contain the proposed locations of NMR oil testing equipment, location of major inspection equipment (e.g., dockage testers and dividers), and a description of the power supply. Any additional information regarding the laboratory setup or equipment should also be discussed.

Where applicable, the monitoring field office will forward a copy of all submitted information to TSD for review. Upon receipt, TSD will review the information and make recommendations to the agency and, where applicable, the monitoring field office to facilitate the laboratory setup.

b. New Equipment.

Notify TSD before placing newly purchased NMR instruments in service. TSD will provide instructions to check the accuracy of the instrument and correct any deficiencies before the instrument is placed into official service. This process may take several days to complete, so contact TSD as soon as possible if problems are identified. Do not use newly purchased instruments for official NMR oil testing until the instrument has been checked and accepted by TSD.

2.5 INSTRUMENT CALIBRATION AND SSS VERIFICATION LOGS

After the instrument has been installed, it must be calibrated and a record maintained of the calibration name, slope, intercept, and correlation coefficient (R^2) along with the date, time, room temperature and operator initials. Attachments 2.1 and 2.2 are examples of the Calibration Log for High Oleic Sunflower and Mid Oleic (NuSun) Sunflower respectively. Routine checks of the calibration accuracy are required, and a record maintained for each calibration of the date, time, room temperature, operator initials, SSS values when tested as market samples, original SSS values, and calculated values for the specific instrument and calibration. Attachment 2.3 is an example of the SSS Calibration Verification for the Bruker and attachment 2.4 is an example for the Oxford. Specific instructions for performing these tasks are contained in Chapter 6 - OXFORD MQC-5 and Chapter 7 - BRUKER MINISPEC 7.5 AND MINISPEC MQ-ONE SEED ANALYZER XL.

Attachment 2.1. NMR High Oleic Sunflower Calibration Log

High Oleic Oil (HO) Sunflower Calibration Log for Model:					**Serial Number:**		
Please record all calibration and re-calibration values in this log.							
Date	Time	Temp.	Slope	Intercept	Correlation R^2 **MUST be > 0.9900**	Name of NEW Calibration	Operator Initials

Attachment 2.2. NMR NuSun (NS) Sunflower Calibration Log

NuSun (NS) Sunflower Calibration Log for Model:					**Serial Number:**		
Please record all <u>calibration</u> and <u>re-calibration</u> values in this log.							
Date	Time	Temp.	Slope	Intercept	Correlation R^2 **MUST be > 0.9900**	Name of NEW Calibration	Operator Initials

Attachment 2.3. NMR SSS Calibration Verification Log for High Oleic (HO) Oil

Instrument ID:_____ Calibration ID: _____ Initial Temp. (°C):_____ Slope: _____ Intercept: _____ R^2: _____

Measure daily, or every 30 – 40 samples, or if the temperature changes by ±1.0 °C.
Tolerance: If measured value exceeds the calculated value by ±0.3%, retest the SSS.
If the measured value still exceeds the CV by ± 0.3% re-calibrate the instrument and retest the SSS.
If re-calibration is needed, update the NMR SSS Calibration Log and fill out new NMR SSS Calibration Verification Log

				Blank SSS		Low SSS		Medium SSS		High SSS		Re-calibration needed
			SAMPLE NUMBER									
			WEIGHT (g)									
			ORIGINAL OIL (%)									
			CALCULATED (CV) OIL (%)									
Date (mm/dd/yy)	Time	Temp (°C)	User Initials	Blank SSS Value (%)	Diff. from CV	Low SSS Value (%)	Diff. from CV	Medium SSS Value (%)	Diff. from CV	High SSS Value (%)	Diff. from CV	

Attachment 2.4. NMR SSS Calibration Verification Log for Mid Oleic (NuSun) Oil

Instrument ID:_____ Calibration ID: _____ Initial Temp. (°C):_____ Slope: _____ Intercept: _____ R^2: _____

Measure daily, or every 30 – 40 samples, or if the temperature changes by ±1.0 °C.
Tolerance: If measured value exceeds the calculated value by ±0.3%, retest the SSS.
If the measured value still exceeds the CV by ± 0.3% re-calibrate the instrument and retest the SSS.
If re-calibration is needed, update the NMR SSS Calibration Log and fill out new NMR SSS Calibration Verification Log

				Blank SSS		Low SSS		Medium SSS		High SSS		Re-calibration needed
			SAMPLE NUMBER									
			WEIGHT (g)									
			ORIGINAL OIL (%)									
			CALCULATED (CV) OIL (%)									
Date (mm/dd/yy)	Time	Temp (°C)	User Initials	Blank SSS Value (%)	Diff. from CV	Low SSS Value (%)	Diff. from CV	Medium SSS Value (%)	Diff. from CV	High SSS Value (%)	Diff. from CV	

CHAPTER 3
SAMPLE PREPARATION

Contents

3.1 BASIS OF DETERMINATION

Determine sunflower seed NMR oil on a representative portion cut from the sample after the removal of foreign material. Report the sunflower seed NMR oil percent on a 10 percent moisture basis (mb).

3.2 CLEANING SAMPLES

Use a Boerner divider to obtain a representative sample portion of approximately 50 to 55 grams. Mechanically clean the sample portion using a Carter Dockage Tester operated as specified in the Grain Inspection Handbook, Book II. Sunflower seeds and dehulled seeds that pass over the riddle and the material that passes over the No. 3 and over the No. 8 sieves are combined to form the mechanically cleaned sample. Handpick the mechanically cleaned sample portion to remove all matter other than sunflower seed and dehulled seeds. Refer to Grain Inspection Handbook II, Chapter 11 for complete definitions of sunflower seed and dehulled seeds.

3.3 PORTION SIZE

The sample used to determine the NMR oil must not extend above the top of the Radio Frequency (R.F.) coil. For a 150-ml NMR sample tube, a depth of 44.45 to 50.8 mm (1 3/4 to 2 inches) must be observed.

Before drying the handpicked sample portion, check the sample volume using a marked NMR sample tube as shown in Figure 3.1. If the sample volume does not fall within the required range, adjust the sample size until it does. If the deviation is large, use a Boerner divider to adjust the sample size.

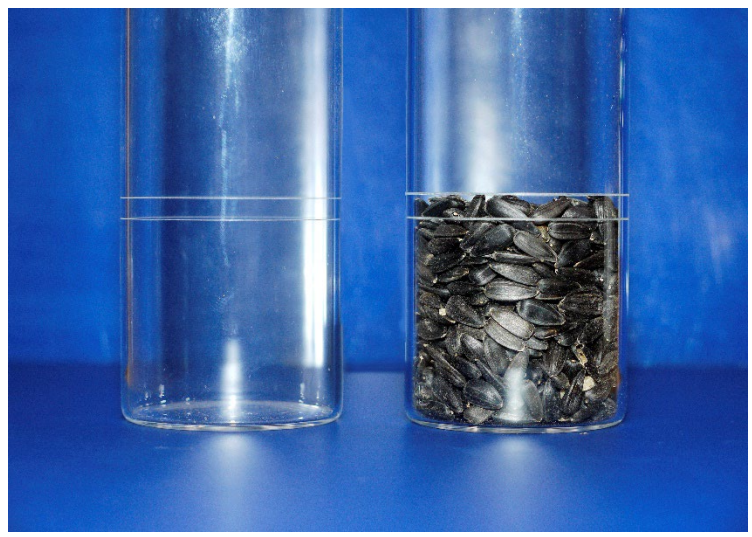

Figure 3.1. NMR Tubes - empty and properly filled.

3.4 DRYING SAMPLES

The technique used to determine sunflower seed oil is based on measuring the number of electromagnetically activated hydrogen atoms in a sample. Therefore, liquid hydrogen atom sources other than oil, such as moisture, must be removed prior to NMR oil determination.

Perform the following procedures for drying the sunflower seed sample to remove moisture:

(1) Preheat the moisture oven to 130°C and check the oven temperature with a calibrated thermometer. The oven temperature must be 130°C ± 2°C before drying samples.

(2) Place the handpicked sunflower seed sample in a moisture dish and record the dish ID number.

(3) Place the sample in the preheated moisture oven with the lid under the dish. Dry the sample for 3 hours. Begin timing the drying once the temperature reaches 130°C ± 2°C.

3.5 COOLING SAMPLES

After drying, the sunflower seed samples must be stabilized to room temperature before performing NMR oil determination. In addition, room and sample temperature must be within ± 0.5°C from the previous temperature recorded on Attachments 2.3 and 2.4.

Allow samples to cool to room temperature using one of the following procedures:

a. Desiccating Cabinet Method.

(1) Place a calibrated thermometer inside the desiccating cabinet.

(2) Immediately after removing the samples from the drying oven, place the lid on the dish and place the dish in the desiccating cabinet. Monitor the desiccating cabinet temperature.

(3) When the room and desiccating cabinet temperature are within ± 0.5°C, samples are ready for NMR oil determination. The cooling time will be a minimum of 3 hours.

b. NMR Sample Tube Method.

A thermometer inserted through a rubber stopper is needed to measure the temperature of at least 1 sample in a rack (maximum 10 samples per rack) as they cool. The thermometer must be inserted into the rubber stopper so that approximately 25 mm of the thermometer will be immersed in the sunflower seed sample during the cooling period.

(1) Immediately after removing each sample from the drying oven, pour the sample into a marked NMR sample tube and seal with a rubber stopper. Each rack must have at least one rubber stopper with a thermometer inserted.

(2) Place the NMR sample tube into a rack. The rack should keep sample tubes separated by approximately 20 mm.

(3) When room temperature and the thermometer reading are within ± 0.5°C, the samples are ready for NMR oil determination. The cooling time will be at least 3 hours.

CHAPTER 4
CERTIFICATION

Contents

4.1 SEED TYPE DECLARATION

Applicants requesting sunflower seed oil determination must declare the seed type as part of the request for service. Written confirmation or a verbal declaration may be required at the discretion of official personnel.

Applicants may make blanket declarations for all lots or a specific type of service. For example, “All inbound lots of sunflower seed are of high-oleic-type unless specified otherwise.”

The official certificate shall include a qualifying statement reflecting applicant declaration (see section 4.3.c).

4.2 EXPORT LOTS

Applicants for service may request official sunflower seed oil determination on the basis of sublot samples or a composite sample. The type of service and the quantity of sunflower seed to be loaded must be indicated on the load order document.

a. Sublot Basis.

(1) Obtain a representative sample for each sublot.

(2) Follow the official procedure to determine NMR oil content for each sublot sample. Record the oil percentage on the inspection log to the nearest tenth percent.

(3) Using the standard FGIS rounding procedures, calculate the average NMR oil content for all sublots.

(4) Determine the highest and lowest NMR oil percent for all sublots.

(5) Report the high, low, and the average percent NMR oil (10 percent moisture basis) to the nearest tenth percent on the certificate.

b. Ship Composite Basis.

(1) Based on the number of sublots being loaded, determine the amount of sample portion (in proportionate size) to be taken from each sublot that will provide a 1,000-gram composite sample.

(2) At the completion of ship loading, obtain a representative sample of at least 100 grams from the composite using a Boerner divider.

(3) Determine the NMR oil content using the official procedures.

(4) Report the percent NMR oil (10% mb), as determined on the composite sample, to the nearest tenth percent on the certificate.

4.3 CERTIFICATION

Record the percent oil of the sunflower seed using the appropriate approved statement in the "Remarks" section of the official grade certificate. Results may be reported on the same certificate with official grade and factor results or reported on a separate certificate. When certifying oil alone (without official grade and factors) do not enter a grade on the “Grade” line.

a. Approved Statements for Export Lots.

(1) Sublot Basis

"Oil content of sublots range from (lowest) % to (highest) %." "Average oil content for all sublots__%, 10 percent moisture basis."

(2) Composite Basis

"Oil content___%, 10 percent moisture basis. Determination based on a composite sample."

b. Approved Statement for Domestic Lots.

"Oil content___%, 10 percent moisture basis."

c. Approved Qualifying Statements.

The applicant for service must declare the type of seed for NMR oil testing. Include one of the following statements on the certificate. Insert the appropriate sunflower seed (mid-oleic, high-oleic) to complete the statement.

Note: The term NuSun may be used in lieu of mid-oleic.

"(_____) type sunflower seed, per applicant statement." "Applicant states sunflower seed is (_____) type."

Field office managers can approve minor modifications to the statements provided the meaning and intent of the statements have not changed.

CHAPTER 5
MONITORING PROGRAM

Contents

5.1 GENERAL INFORMATION

The sunflower seed oil monitoring program is designed to monitor the accuracy of official sunflower seed oil determinations. Several methods are utilized to monitor particular elements in the sunflower seed oil testing process. These methods include monitoring by TSD, check samples, intermarket sample exchanges, and special studies or collaboratives.

Monitoring information is used by field offices and/or inspection agencies for evaluating the performance of their local oil testing programs. TSD uses the information to evaluate the capability of the national sunflower seed oil testing program and the performance of the calibration standards.

Monitoring by TSD will identify service points having questionable oil results. Field offices and/or agencies must initiate follow-up and corrective action whenever oil testing problems are detected. Follow-up and corrective actions include investigating, identifying, and correcting oil problems. Intermarket sample exchanges, opinion samples, and special studies or collaboratives, are tools which are used to help identify the cause of discrepancies. TSD will assist the field in identifying the cause(s) of oil testing problems.

5.2 MONITORING FILE SAMPLES

Oil testing performance is evaluated through TSD monitoring of official file samples. Sunflower seed oil program performance is determined by comparing original NMR oil results with monitoring results.

Official Service Providers (OSP) are required to select and forward 10 samples monthly to TSD for monitoring, for each SSP where sunflower oil testing was performed.

a. Selecting Samples.

OSP shall use the following procedures to select monitoring samples for each SSP providing official NMR oil testing service.

NOTE: Do not select all monitoring samples from the same day.

(1) Select 10 sunflower seed samples (file sample and NMR portion) per month representing the range of oil values observed during the month. Do not select all samples from the same day. When less than 10 samples are tested during a month, select all samples tested.

(2) OSP with SSP that perform a low volume of official oil determinations may, with TSD concurrence, periodically make up sets of 10 samples to check the accuracy of their instrument.

(3) Ship the samples to TSD by close of business on the last business day of the month.

Note: TSD may request additional samples for monitoring and/or troubleshooting purposes.

b. Preparing Samples.

(1) Using a Boerner divider, obtain a portion weighing approximately 200 grams from each sample selected for monitoring. If a location frequently receives submitted samples of insufficient size to provide a 200-gram portion, TSD may approve a smaller monitor portion.

(2) Place each sample portion in a clear plastic bag and close securely.

(3) Include a completed NMR monitoring data worksheet with the samples. Indicate any unusual conditions observed in the "remarks" section of the worksheet. Refer to Attachment 5.1 for a printable version.

c. Packaging Samples.

(1) Place the selected sample portions and completed monitoring data worksheet in a suitable mailing bag or box.

(2) Prepare the samples for shipping using the appropriate shipping method and label the box as "SF Oil Monitoring". Contact TSD for shipping information.

d. Monitoring Results.

TSD will prepare summary reports and transmit the SSP sunflower seed oil monitoring results to the appropriate OSP for their review and follow-up action.

e. Evaluating Results.

TSD and OSP managers are responsible for evaluating the monitoring results. If the results indicate unacceptable performance, they must initiate follow-up action, take the necessary corrective measures, and document any action taken to resolve differences between original and monitoring data.

Documentation may be placed directly on the report, in a ledger or notebook, and must indicate the nature of the problem and the corrective action taken.

Attachment 5.1. NMR Monitoring Data Worksheet

Location:	
W/E:	
Date of Analysis:	
Operator:	

NMR Monitors					TSD Use Only			
					Date Analyzed:		*Operator:*	
#	**Sample ID**	**Oil Type**	**SSP Oil%**	**Weight**	*Tin ID*	*Dry Wt.*	*Bruker*	*Oxford*
1								
2								
3								
4								
5								
6								
7								
8								
9								
10								

NOTE: W/E is week ending date. SSP Oil is the oil percent results from the official agency/field office.

REMARKS:

5.3 CHECK SAMPLES AND SPECIAL STUDIES

Check samples may be issued by TSD periodically to identify potential intermarket differences between service points, and to track the capability of the national oil testing program in relation to the reference method. Special studies are designed to resolve differences in oil results either within or between markets.

a. Check Samples.

TSD will select bulk samples of sunflower seeds representing the range of oil values typically seen in the market and prepare multiple sets of representative portions. On an as-needed basis, a portion of each of these samples will be distributed to SSP, FGIS field offices, and the TSD reference method lab to be tested for oil content. Participants must complete the oil testing within 7 working days of receipt of the samples and transmit the results to TSD.

TSD will tabulate, plot, and analyze the data and prepare a report of the average results of all locations compared to TSD. Plots and statistical analysis will be transmitted to all participants and supervising FGIS offices.

DIOO and/or SSP managers must initiate corrective action and follow-up when needed. The TSD will assist the field offices in resolving intermarket differences and investigate and take necessary action when excessive differences between the NMR oil and reference methods are indicated.

b. Special Studies or Collaboratives.

Special studies or collaboratives, conducted at the discretion of TSD, are designed to resolve differences in NMR oil results within or between markets. Because special studies are normally of an urgent nature, an expedient resolution of the problem is essential. Therefore, all participants must perform the requested tests and report the results to TSD within 5 working days.

5.4 INTERMARKET SAMPLE EXCHANGE

An intermarket sample exchange is used to isolate oil differences between inspection points. Oil testing laboratories will determine oil results on separate portions obtained from the same sample. Oil results are then compared to determine whether significant differences between locations exist. This procedure is particularly useful when there are sunflower seed shipments between two SSP or an individual applicant is routinely receiving service from two service points.

There are no restrictions as to which offices may exchange samples. SSP are encouraged to exchange samples with other service points for the purpose of investigating and resolving intermarket inspection differences. A copy of the results of the exchange must be provided to TSD for review.

CHAPTER 6
INSTRUMENT SETUP AND SAMPLE ANALYSIS – OXFORD MQC-5 PULSED NMR ANAYZER

Contents

6.1 INSTRUMENT SETUP

Operators must read the user's manual and familiarize themselves with this instruction before operating the NMR instrument. The operation of the OXFORD MQC-5 pulsed NMR instrument is controlled by the electronics unit which includes a built-in computer. After the instrument is powered on, a series of automatic internal tests are carried out to confirm proper instrument functionality. Any error messages should be referenced in the user's manual.

The magnet is maintained at a temperature of 40 degrees Celsius (°C). The unit must not be used for a period of 6 hours after being powered on to allow the magnet temperature to stabilize. After being powered-on the instrument should remain on.

After the instrument is powered on, open the "MQC System Setup" icon on the desktop. A series of tests will be carried out to confirm the instrument communications and the functionality of the console unit. Please follow all computer prompts and consult the MQC-5 user manual "Section 4 – Using the Instrument" for any questions. The setup process may take up to 24 hours.

6.2 INSTRUMENT CALIBRATION

The NMR instrument must be calibrated, using the FGIS Sunflower Seed Standards (SSS). The instrument software supports a four-point calibration. The points will be the high, medium, low, and blank valued SSS. Once the instrument has been calibrated, the instrument calibration is verified daily prior to use, every two hours, after 30-40 samples have been analyzed, or when the room temperature changes by ± 1.0ºC.

Follow the procedures listed below for calibrating instruments.

(1) Double click the "EasyCal Applications" icon on the desktop.

(2) Select "Oil Content in Seeds" application. In the window at the top right-hand corner, verify the magnet temperature is at 40.0°C.

(3) Name the new calibration: (FGIS[NS or HO]MMDDYY) where "[NS or HO]" is an abbreviation of the class (NS for NuSun, or HO for high oleic), "MM" is the month, "DD" is the day, and "YY" is the year.. An example of this would be FGISNS050922, indicating that the calibration is for NuSun seed created on May 09, 2022.

(4) Record the new filename on both the NMR Calibration Log (either Attachment 2.1 or 2.2 of Chapter 2, as applicable) and on a new NMR Calibration Verification Log (either Attachment 2.3 or 2.4 of Chapter 2, as applicable).

(5) Click "Start".

(6) Following the prompts, insert the oil tuning sample for analysis. Remove the tuning sample when prompted.

(7) Click "Continue".

(8) Following the prompts, insert the high oil SSS for optimizing. Remove the high oil SSS when prompted.

(9) Enter the Sample ID, mass and oil percent for the high oil SSS with the information provided on the label.

(10) Click “Ok”.

(11) Following the prompts, insert the high oil SSS sample for analysis.

(12) Remove the high oil SSS when prompted.

(13) Click “Yes” when asked to scan another standard.

(14) Repeat steps (9) through (13) for the medium, low and blank SSS standards.

(15) Click “No”, when asked to scan another standard.

(16) Click on “Automatic Calibration” to complete the calibration process

(17) After the computer calculates the calibration parameters, record the slope, intercept, correlation coefficient (R^2) (found in the upper right-hand corner of the screen), room temperature to 0.1°C on the both the NMR Calibration Log and on the new Calibration Verification Log.

(18) The correlation coefficient must be greater than 0.9900. If not, a new calibration will be needed. Repeat steps (3) through (17) again using a new calibration name following this format: FGIS[NS or HO]MMDDYYx where “x” is the number of the recalibration (1 for the first recalibration, 2 for the second recalibration, etc.). Contact TSD if the correlation coefficient is not greater than 0.9900 after recalibration.

(19) Click on “Exit” then confirm by clicking “Yes”. Exit out of any remaining unnecessary windows.

(20) Go to the following folder: [COMPUTER/OS(C):/PROGRAMFILES/RESONANCE/RICALIB/CALIBRATION] and find the file with the calibration name you just created with the “.cd” extension.

(21) Double click to open the file and record the calculated oil% values of the SSSs into the NMR Calibration Verification Log.

(22) Close the file when done: click “Yes’ to “TERMINATE RI CALIBRATION?”.

6.3 DAILY INSTRUMENT TUNING AND CALIBRATION VERIFICATION

The instrument tuning is performed daily before use and the calibration verification is performed daily prior to use or when the room temperature changes by ± 1.0ºC or after every 30-40 samples have been analyzed or every two hours of continuous use, whichever comes first.

Test the SSSs as a sample to check the NMR instrument calibration accuracy. Maintain a record (electronic or written) of the calibration verification using the applicable Calibration Verification Log Found in Attachment 2.3 or 2.4 of Chapter 2.

a. Daily Instrument Tuning.

(1) Select the applicable Calibration Verification Log based on the oil seed type that is being verified.

(2) Complete the header information on the log. Also fill in the date, time, temperature and user initials.

(3) Double click the “RI Analysis” icon located on the desktop and select the appropriate calibration curve, depending on which oil type is to be analyzed.

(4) Click “Start”

(5) Insert the oil tuning sample when prompted.

(6) Remove the oil tuning sample when prompted.

b. Calibration Verification Using the SSS.

(1) When prompted, enter the sample ID for the high oil SSS standard, mass and any comments, then click “OK”.

(2) When prompted, insert the high oil SSS. The instrument will automatically begin the analysis.

(3) When prompted, remove the high oil SSS.

(4) Record the oil value and the room temperature to 0.1°C on the Calibration Verification Log and calculate the difference between the reported and calculated value for the SSS.

(5) Repeat steps (1) through (4) for the medium, low and blank SSS standards.

(6) Determine the difference between each SSS result obtained and the corresponding Calculated Value and record this value on the applicable Calibration Verification Log. If the difference for any SSS exceeds ± 0.3 retest it. If the difference still exceeds ± 0.3%, recalibrate the instrument following the procedures in section 6.2 and perform a new calibration verification using a new Calibration Verification Log.

(7) If the difference still exceeds the tolerance, contact either TSD or Oxford for technical support.

(8) Once the instrument is calibrated, and the Daily Instrument Tuning/Calibration Verification has been completed, begin analyzing samples according to the Section 6.4.

6.4 ANALYZING SAMPLES

Prior to analyzing samples, instrument tuning and the calibration verification should be completed according to the Section 6.3.

a. Testing Samples.

The sample portion used to determine the NMR oil for the Oxford MQC-5 must not extend over 50 mm in height using a 51-mm diameter NMR tube.

(1) If you are already in analysis mode, click “Start” and go to step 6. If not, double click the “RI Analysis” icon located on the desktop to open the program.

(2) Choose the appropriate calibration for the sample being tested.

(3) Click “Start”.

(4) Insert the oil tuning sample when prompted.

(5) Remove the oil tuning sample when prompted.

(6) Enter the sample ID.

(7) Enter the sample mass and click “Ok”.

(8) When prompted insert the sample. The instrument will automatically begin the analysis.

(9) Remove the sample when prompted.

(10) Record the percent oil.

(11) Repeat steps (6) through (10) for any additional samples of the same seed type.

(12) For samples of a differing seed type, click on “Cancel”. Click on “Exit” then confirm by clicking “Yes”. Double click the “RI Analysis” icon, choose the appropriate calibration for the sample being tested.

(13) Repeat steps (3) through (11).

NOTE: To repeat the analysis of a single sample, you must remove the sample from the magnet and allow it to equalize to room temperature (10-15 minutes). Repeat analysis steps (6) through (10) when the sample has returned to room temperature.

b. Reporting Results.

Record and report the percent oil on the pan ticket, inspection log, and certify to the nearest tenth percent using the standard FGIS rounding procedures.

CHAPTER 7
INSTRUMENT SETUP AND SAMPLE ANALYSIS – BRUKER MINISPEC 7.5 ANS MINISPEC MQ-ONE SEED ANALYZER XL PULSED NMR ANALYZERS

Contents

7.1 INSTRUMENT SETUP

Operators must read the User's Manual and familiarize themselves with this instruction before operating the NMR instrument. The operation of the Bruker Minispec 7.5 and Minispec MQ-One pulsed NMR instrument is controlled by a personal computer. After the instrument is powered on, a series of tests are carried out to confirm the instrument communications and the functionality of the console unit. Any error messages should be referenced in the User's Manual.

The magnet is controlled at a temperature of 35.5 degrees Celsius (°C) for the Minispec 7.5 and 40.0 °C for the MQ-ONE. The unit must not be used until magnet is at the appropriate temperature. Consult the User's Manual for the proper indication of magnet temperature. This may take up to three hours. After the instrument is powered on, open the minispec software on the computer. Please follow all computer prompts and consult the User's Manual "Section 2.2 – Connecting the PC to the minispec for the (Very) First Time" through "Section 2.4 – Configuration of the Software, the Welcome Box".

7.2 INSTRUMENT CALIBRATION

The NMR instrument must be initially calibrated, using the FGIS Sunflower Seed Standards (SSS). The instrument software supports a four-point calibration. The points will be the high, medium, low, and blank valued SSS. Once the instrument has been calibrated, the instrument calibration is verified daily prior to use, every two hours, after 30-40 samples have been analyzed, or when the room temperature changes by ± 1.0ºC. Follow the procedures listed below for calibrating instruments.

(1) Start the Minispec Plus software and enter the User ID and Password, if necessary. If a Daily Check has not been performed for the day, see Section 6.3 a.

(2) Click on the "Calibrate" button, opening the "Available Calibrations" window. Click the "New Calibration" button at the bottom left of the window.

(3) Name the new calibration FGIS[NS or HO]MMDDYY where "[NS or HO]" is an abbreviation of the class (NS for NuSun, or HO for high oleic), "MM" is the month, "DD" is the day, and "YY" is the year. An example of this would be FGISNS050922, indicating that the calibration is for NuSun seed created on May 09, 2022.

(4) Record the new calibration filename on both the NMR Calibration Log (either Attachment 2.1 or 2.2 of Chapter 2, as applicable) and on a new NMR Calibration Verification Log (either Attachment 2.3 or 2.4 of Chapter 4, as applicable).

(5) Also fill in the header, record the date, time, temperature, and operator initials on both Logs.

(6) Select the "Bruker Oil in Seeds" application. Change the reference values to "Mass Percent" and click "Apply". Click the "Calibrate" button and you will be prompted to insert the high oil SSS to tune the receiver gain but do not insert the SSS. Click on "Tune Gain" and insert the high oil SSS when prompted. Once completed, the calibration procedure screen will appear and remove the SSS.

(7) Provide the sample name (SSS###), sample mass, and sample reference values (percent oil of the SSS) from the SSS label.

(8) Click “Measure” and wait for the prompt “Please Insert Sample” before doing so.

(9) When the analysis is complete, remove the high oil SSS. Press “Next Sample” if another standard or the blank needs to be measured.

(10) Repeat steps (8) through (10) for the medium, low, and the blank SSS standards.

(11) Once completed, click on “Calibration Results”. The calculated values will be displayed; record these values on the NMR Calibration Verification Log.

(12) Next, click on “Show Calibration”. A graph and calibration statistics will be displayed. Record the slope, intercept, correlation coefficient (R^2), on both the NMR Calibration Log and the NMR Calibration Verification Log.

(13) The correlation coefficient must be greater than 0.9900. If not, a new calibration will be needed. For a new calibration, click on “Return to Main Menu” and repeat steps (1) through (10) again using a new calibration name following this format: FGIS[NS or HO]MMDDYYx where “x” is the number of the recalibration (1 for the first recalibration, 2 for the second recalibration, etc.). Contact TSD if correlation coefficient is not greater than 0.9900 after recalibration.

(14) If the calibration is acceptable, click “Sign” to accept the calibration. Enter any password information if required. The calibration will not be available for use without signing.

NOTE: If an error message is displayed, contact Bruker technical support.

(15) Click “Return to Main Menu” to perform a calibration verification.

7.3 DAILY INSTRUMENT CHECK AND CALIBRATION VERIFICATION

The instrument check is performed daily before use and the calibration verification is performed daily prior to use or when the room temperature changes by ± 1.0ºC or after every 30-40 samples have been analyzed or every two hours of continuous use, whichever comes first.

a. Daily Instrument Check.

The following procedures are used at the start of the day to verify the instrument is tuned and ready for use.

(1) If not already open start the Minispec Plus software and enter the User ID and Password, if required.

(2) Click the “Daily Check” button, then click “start”.

(3) When you see the prompt, “Please Insert Check Sample”, insert it then press “ok”.

(4) The instrument will perform a series of tests. If no error message appears, you are done; remove the check sample. It is ready for use.

(5) The Daily Check need not be recorded because it is logged internally

(6) If an error message occurs, an error message appears, select “Update Settings” from the Minispec menu, and click “ok” to proceed to update all instrument settings.

(7) After the instrument updates the settings repeat the Daily Check. If the instrument repeatedly fails the Daily Check, contact technical support at Bruker for assistance. After use of the “Updated Settings”, all previous calibrations become void, and the instrument needs to be recalibrated.

b. Calibration Verification Using the SSSs

Test the SSSs as if they were a sample to check the NMR instrument accuracy. Maintain a record (electronic or written) of the calibration checks using the applicable Calibration Verification Log Found in Attachment 2.3 or 2.4 of Chapter 2.

(1) Select the applicable Calibration Verification Log based on the oil seed type that is being verified.

(2) Complete the header information on the log. Also fill in the date, time, temperature and user initials

(3) Select the “Measure” button and a new window will appear.

(4) Provide an appropriate batch name. This can be any identification the operator or location determines is appropriate. Press the enter key.

(5) Select the appropriate calibration being used. For a new calibration, you may need to type in the name before it will appear.

(6) Enter the sample name, sample mass, and any comments, then click “Measure”. When the prompt, “Please Insert Sample” appears, do so.

(7) When the analysis is completed remove the SSS and record the oil value on the Calibration Verification Log.

(8) Calculate the difference between the reported and calculated value for the SSS. If the difference exceeds ± 0.3 from the calculated value, repeat the analysis. If the repeat analysis result difference still exceeds ± 0.3, recalibrate the instrument.

(9) Repeat steps (6) through (8) for the medium, low, and blank SSS standards. If needed, click on “Next Sample”.

(10) Click on the return arrow button to exit.

7.4 ANALYZING SAMPLES

Prior to analyzing samples, instrument daily check and the calibration verification should be completed according to the schedule in Section 7.3

a. Analyzing Samples.

(1) Select the “Measure” button.

(2) Provide an appropriate batch name, which is any identification the operator or location determines is appropriate.

(3) Select the appropriate calibration for the sample being tested.

(4) Enter the sample name, mass, and any desired comments.

(5) Click the “Measure” button, then wait for the prompt, “Please Insert Sample”, before inserting the sample.

(6) When the measurement is complete, remove the sample from the magnet and record the percent oil value. Click on “Next Sample” if needed.

(7) Repeat steps (4) through (6) for the remaining samples of the same seed type. For samples of a differing type, press the return arrow button and repeat steps (1) through (6).

NOTE: To repeat the analysis of a single sample, remove the sample from the magnet and allow it to equalize to room temperature (10-15 minutes). Repeat analysis steps (4) through (6) when the sample has returned to room temperature.

b. Reporting Results.

Record and report the percent oil on the pan ticket, inspection log, and certify to the nearest tenth percent using the standard FGIS rounding procedures.

CHAPTER 8

REVISION HISTORY

Contents

CHANGE NO. 4: SEPTEMBER 30, 2022

This update superseded the FGIS Nuclear Magnetic Resonance (NMR) Handbook dated October 1, 2009. This handbook was revised and reformatted to incorporate FGIS's move to AMS, minor process changes, updated forms, inclusion of FGIS PN 14-04 Approval of New Nuclear Magnetic Resonance (NMR) Instruments (11/21/2013):

Chapter 1 - 1.2 Added multiple definitions.

Chapter 2 - Updated Attachments 2.1, 2.2, 2.3, and 2.4.

2.2, Updated the approved NMR instruments.

Chapter 5 - Updated Attachment 5.1

5.2 Updated the number, type, and frequency of NMR monitoring file samples.

5.3 and 5.4 Updated sections.

Chapter 6 - New Chapter for Oxford MQC-5 NMR setup and operation.

Chapter 7 - New Chapter for Bruker Mini Spec 7.5 and MQ-One Analyzer XL setup and operation.

CHANGE NO. 3: OCTOBER 1, 2009

This update superseded the FGIS Nuclear Magnetic Resonance (NMR) Handbook dated May 12, 2003. This handbook is updated to reflect organizational changes in the monitoring system, procedural changes, instrument changes, and a change in certification to compliment CRT.

CHANGE NO. 6: MAY 12, 2003

The Nuclear Magnetic Resonance (NMR) Handbook was revised to include procedures for testing sunflower seed oil with pulsed wave NMR instruments (Oxford MQA 6005 and MQA 7005, Resonance MARAN Ultra, and Bruker Minispec 7.5). Additionally, the instructions for selecting monitoring samples have been revised to reflect current selection criteria.