of buyers and sellers of oilseed products enroll solely to maintain and to verify their own analytical proficiency. Independent chemists–those who do not work for buyers or sellers of oilseeds or oilseed products–who do well enough in the Smalley Program can be certified as AOCS official referee chemists. Applicants must be AOCS members whose labs have been inspected to ensure the labs are properly equipped to perform AOCS analytical methods.

Trade associations' "official chemists" serve as objective arbitrators or mediators to help resolve disputes about product quality. If analysts for buyer and seller agree on quality, there is no problem. If they disagree, a mutually selected "official chemist" can provide an objective analysis. Although the official chemist's analysis may be binding, the disputants also may use it as the basis for further negotiating. Thousands of dollars in a single soybean oil sale may hinge on analytical discrepancies. Buyers and sellers both must have confidence in the method used to resolve disputes.

Let me again state that the Smalley Program is viable and urge your inspection of and participation in several series of samples.

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Quality Control in Processing Drying Oils

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ABSTRACT

A brief history of linseed oil, its production trends, uses and prospects for the future are discussed. Methods of processing, effects of process variables on oil quality, how quality is measured and how it is maintained are the main topics of this paper. Although linseed oil production declined steadily for many years after World War II, it has stabilized in recent years and shortages of petroleum products could cause a return to linseed oil in the form of water emulsion. Brief references to other drying oils will be included. Quality control begins with seed quality and includes storage, cleaning, processing and degumming. Refined oils described include alkali-refined, blown, heat-bodied and chemically modified oils. Present quality control methods are described. Problem methods such as the "foots" test for degummed oils are described. Recent developments used on occasion included liquid chromatography, thin layer chromatography (TLC), ultraviolet (UV) and infrared (IR) spectroscopy, but the most predominantly used technique has been gas chromatography (GC). Recent developments in capillary GC and fused silica columns have improved separations and reduced analysis times. Near infrared reflectance shows some promise for future quality control work.

INTRODUCTION

Many years have passed since the subject of drying oils (1), and many more years since quality control in drying oils, has been a topic at an AOCS annual meeting (2). One might well ask: in view of current production volumes, who cares?

There are some reasons for hope for the future of drying oils. Renewable resources can supply virtually all the raw materials needed for making coatings if and when petroleum is no longer available (3). The major source of traditional agricultural raw materials for coatings is the seed oils. Alkyd resins are the major market for the seed oils, with linseed, soybean and sunflower the principal oils used in alkyd resin technology. Future price increases or petroleum shortages may add impetus to the development of substitutes for petroleum-based monomers and polymers for coatings. In recent years, vegetable oils were replaced by the, then, less expensive petrochemicals, but now vegetable oils may need to be reconsidered. Linseed oil paints, in water emulsion form, with their well known performance advantages, are ready and waiting to be rediscovered. Several long oil emulsifiable linseed alkyds have been developed and paints using them have been formulated and evaluated. Test fence data looked promising. The well known advantages of linseed oil for exterior coatings are retained and the clean-up advantages of latex coatings are added. The coatings industry showed little interest when crude oil was $3.00 per barrel, but this could change in the future.

Drying oils include linseed oil, tung oil, castor oil and oiticica oil. Since the early 1970s, only linseed oil is shown in US production figures. Small quantities of the others are still imported for specialty uses. These include alkyds, urethanes and varnishes. Many of the control methods used for linseed oils apply to the other drying oils as well.

Foreign linseed oil production is down about 25% over the past 10 years (4,5), but showing signs of leveling out. Domestic production has declined about 75% over the same period, from 27% of total world production to about 6% of the total production. This, too, shows signs of stabilizing, thus providing a base for any future expansion of production.

The topic of this paper is quality control in drying oils, although a valid assumption is that US linseed oil plants and refineries are multi-product plants and probably have frequent product changes. Therefore, product separation and purity become all-important and the quality control function is a key one. Multi-product plants must be monitored throughout all parts of the process. Lines, storage, blending, loading and shipments must be checked for contamination.

By far the most important quality control tool is gas chromatography (GC); we could not operate a plant without it. Recent developments provide good separation with easy-to-use columns (fused silica Wall-Coated Open Tubular [WCOT]) and elution of the linolenic ester in less than 5 min. This means a sample can be analyzed in 30 min, including methyl ester prepartion, chromatographic separation and calculation of results with the improved electronic integrators available today.

The most frequently used control methods are those of AOCS, ASTM, AACC, AOAC and IUPAC. The first two are most frequently used. Table I lists the AOCS methods most frequently used in quality control of drying oils. These methods are constantly being evaluated by participants in the Smalley Check Series Program, a very valuable tool with which to evaluate methods and laboratories.

Raw linseed oil is usually sold on the basis of ASTM methods, Part 29, shown in Table II. These methods are

TABLE I

AOCS Method S 2-64—Recommended Practices for the Testing of Drying Oils[a]

Test	AOCS method
Sampling	Ta-1
Acid value	Te-2a
Iodine value	Tg-1
Diene value	Th-1a
Dienoic acids	Ti-1a
Saponification value	Tl-1a
Unsaponifiable matter	Tk-1a
Ash	Tm-1a
Acetone tolerance	Tt-1a
Color	Td-1a
Specific gravity	To-1b
Refractive index	Tp-1a
Viscosity	Tq-1a
Dry time	No method
Flash point	Tn-1a
Nonvolatiles (solids)	Tc-1a
Clarity	No method

[a]This method covers the selection and use of procedures for testing drying oils commonly used in paints, varnishes and related products. The test methods included are listed in Table I.

TABLE II

Properties of Raw Linseed Oil ASTM D234

Property	Requirement	ASTM method
Specific gravity, 25/25 C	0.926-0.931	D 1963
Acid value, max.	4.0	D 1639
Saponification value	189.0-195.0	D 1962
Unsaponifiable matter, max. %	1.50	D 1965
Iodine value (Wijs), mon.	177	D 1959
Loss on heating at 105-110 C, max. %	0.2	D 1960
Appearance	clear and transparent at 65 C	
Color (Gardner), max.	13	D 1544
Foots, volumetric, heated oil, max. %	1.0	D 1954
Foots, volumetric, chilled oil, max. %	4.0	D 1954
Gravimetric foots, max. %	0.25	D 1966
Flash point, min., degrees F	250	D 1393

subject to revision at any time and must be revised, reapproved or withdrawn every 5 years by the appropriate technical committee of the ASTM.

SPECIAL METHODS

Linseed oil processing evolved differently from most edible oils. Many crude oil plants evolved in the edible oil industry, produced crude oils and shipped these to refiners who completed the processing. Producers and refiners learned how to handle the crude oils and the gums. Linseed oil, however, was supplied to coatings manufacturers as raw oil, in smaller amounts, and held in storage for longer periods. Hence, tank settlings became a problem. Crude oil was not suitable for the coatings trade, so degummed oil became the oil of commerce. The consumer wanted a test which would predict the amount of tank settlings, do it simply, with one test, and without expensive equipment or extensive technical expertise. The ASTM Volumetric Foots Test D 1954 was the result. It does all of the above, some of the time, but reproducibility, both within and between labs, is poor.

The Volumetric Foots Test was studied extensively by ASTM with the aim of improving or eliminating it. An acetone-KI method, Nephelos test (turbidity), wax tests and phosphatide content were all studied. A gravimetric method or phosphoric acid-treated (PAT) foots test was developed and accepted by ASTM. It is used as a trading specification by some customers but has some disadvantages. It is time consuming, requires considerable operator skills and does not describe completely the nature of the tank settlings; the Volumetric Foots Test thus remains as a part of ASTM specifications. The old Volumetric Foots Test is still used by processors because, if you understand it, it can serve as a convenient test for describing oil quality, even though it is often an unfair basis for trading purposes. It describes adequately top quality oils and poor quality oils with a fair degree of reliability but is entirely unsatisfactory for describing oils between these extremes.

Nuclear Magnetic Resonance (NMR) analyzers are used extensively for determining oil content of sunflower seeds (6). Sunflowers are traded on the basis of oil content. Since sunflowers and flax are usually processed in the same plants, NMR is usually available as an analysis tool for flax processors. It can be used for determining oil content of flaxseed and for determining oil content of expeller cake. The manufacturers claim it can be used for spent flakes and meal. Published data on the use of NMR to determine residual oil in spent flakes and meals is scarce.

REFINING AND BLEACHING

Drying oils for alkyds have traditionally been alkalai-refined and bleached. Quality control consists of insuring the removal of most of the waxes and complete removal of phosphatides to 5 ppm phosphorus or, preferably, less than 2 ppm. Operating procedures in the multi-product plants designed to produce quality edible oils will also produce good quality refined linseed oil provided it is refrigerated and filtered or centrifuged to remove the waxes. Low dockage content in the seed must be maintained and is monitored by checking for dockage on a regular basis and cleaning the seed to acceptable levels, and by heated color determination on both raw and refined oils. Vacuum bleaching produces good colors and good bleached colors. These are normally measured by the Gardner color method but useful information is also provided by the Lovibond method. Soap and phosphatide contents must be low for edible oils and are beneficial for drying oils as well, particularly those used in alkyd manufacture. The capability for producing high quality drying oils exists today more than ever before.

STEAM REFINING

Steam refining has become more popular in recent years. This certainly has potential for linseed oil. Cold degumming with or without acid pretreatment (dependent on the level of residual phosphorus), followed by steam refining, can produce a good quality oil with a small neutral oil loss and with a better quality fatty acid residue. Phosphorus content becomes a very important test for this process because certain abused oils (e.g., moldy seed or overheated still) do not respond to this process and must either be alkali refined or sold as raw oil.

FUTURE QUALITY CONTROL

An instrument utilized for protein, fat, moisture and crude fiber contents of cereals and other dry products has recently been modified with a liquid cell. Near infrared reflectance (NIR) has been used for several years but the liquid cell enables the measurement of moisture, fatty acids, iodine value and perhaps neutral oil loss, with little or no sample preparation. This technique holds considerable promise but must be thoroughly evaluated. As processors increase their production volumes, they will need to become more sophisticated in their process quality control in order to remain competitive. This means more samples analyzed and probably more instrumental analysis, using the classical wet methods as reference methods for calibrating instruments, rather than as routine methods.

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Quality Control in a Canola Crushing Plant

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ABSTRACT

A strong emphasis on quality control provides the technical base on which the reputation for the oil and meal products from a crushing plant is established. Most crushing plants in Western Canada now process only canola, the new quality oilseed developed from the former rapeseed. Quality control procedures employed by these plants to contract, grade, purchase and segregate canola seed for processing are described. Quality products are manufactured to meet national standard specifications of quality with the aid of a regular schedule of sampling and laboratory analysis, combined with frequent communication between quality control personnel and plant operators. Operating procedures are established to minimize variability in the quality of oil and meal products resulting from the natural variation in the characteristics of the seed to be processed. Instrumental methods of analysis are being used increasingly to facilitate the analysis of process materials.

INTRODUCTION

Vegetable oils are extracted from a wide variety of oil-bearing seeds and fruits in crushing plants ranging in size from a few tons per day to over 3,000 tons of seed per day. The unique physical and biochemical characteristics of individual species of seed or fruit have often necessitated the development of unique extraction processes for each. In addition, distinct national or cultural preferences in the quality of edible fat and oil products have developed in certain countries which have resulted in further specialization of processing parameters and equipment. The subject of quality control in crushing plants, therefore, covers a very broad field of interest. In this paper, the scope of the discussion will be confined to quality control in the processing of canola seed grown and processed in Canada.

Canola seed is a genetically engineered oilseed, developed in the 1960's and 1970's from the traditional rapeseed. Rapeseed, as it is known in world commerce, is a heterogeneous mixture of several distinct Brassicae species including *Brassica Napus, B. Campestris, B. Juncea, B. Sarson* and others. The composition of oil and meal components of the naturally occurring land races from each specie are known to differ in several important respects, i.e., fatty acid composition, protein content, hull color and the amount and composition of glucosinolates (1). These differences were further highlighted with the genetic isolation of seed within the *B. Napus* and *B. Campestris* species containing low levels of erucic acid and low levels of certain glucosinolates (2). With these latter developments, a new oilseed was created which, when processed, yielded oil and meal products uniquely different to products from the traditional rapeseed and mustards.

The name canola is the registered trademark of the Canola Council of Canada and may be used freely to reference the seed, oil and meal products obtained from *B. Napus* and *B. Campestris* containing less than 5% erucic acid and less than 3 mg/g glucosinolates. Glucosinolates included in this specification are only those which have been commonly analyzed to date, i.e., gluconapin, glucobrassicanapin, progoitrin and napoleiferin. Their contents are expressed in units of mg equivalents of 3-butenyl isothiocyanate released per gram sample (meal basis) or, more appropriately, as micromoles glucosinolates per gram sample (3 mg/g $\simeq$ 26 micromole/g).

QUALITY CONTROL OF SEED FOR PROCESSING

Brassicae species currently grown in Western Canada are of the summer form of *B. Napus* and *B. Campestris.* In 1981, over 85% of the Brassicae varieties grown were of the canola type. Very recently, agronomic and plant breeding research was initiated to develop also winter canola varieties of *B. Napus* adapted to Southern Ontario. The general seed characteristics and yield relationships between the summer and winter types, when grown in Canada, are expected to be similar to those described recently for summer and winter biotypes grown in Europe (3).

The production and quality of canola grown in Canada is surveyed annually by the Canadian Grain Commission and is reported in an annual crop bulletin (4). These harvest surveys show that the erucic acid content of the oil has exhibited a consistent decline during the 1970s. Recent analysis for seed grown in 1981 indicates that canola oil obtained from commercial seed contains 0.5-2.0% erucic acid. Several new varieties are being released currently through the pedigree seed system which have erucic acid contents substantially below 0.2%.

The content of common glucosinolates in seed now also exhibits yearly declines following the release of the first low glucosinolate variety in 1974. Commercial seed in 1981 was found to contain about 3 mg/g of common glucosinolates. Further decreases in the glucosinolate content in the 1982 and 1983 crops occurred as the recently licensed canola varieties Tobin, Andor and Westar entered the commercial production system and completely replaced the remaining high glucosinolate varieties still in production.