OIL QUALITY ANALYSER.

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ABSTRACT

Environmental conditions strongly influence the degree of unsaturation of sunflower oil. Conventional analytical methods for oil quality assessment can be expensive and time consuming. The mathematical relationship between refractive index and the degree of unsaturation of sunflower oil has been used to develop an analytical instrument which, after injection of a sample oil, automatically displays the refractive index (25°C), iodine value, % linoleic acid and % oleic acid of the oil. Refractive index is measured using a differential refractometer by comparison with a reference oil. Calculation of results, control of the digital displays and continual updating, are microprocessor controlled. Stable results are displayed within two minutes of sample injection (1 ml). The instrument is designed primarily for sunflower oil but has some application for related oils.

INTRODUCTION

Until recent times, the refractive index of a vegetable oil was one of the most used specifications for oil quality. This value provided a useful guide to the degree of unsaturation of the oil and was often accompanied by the chemically determined iodine value or iodine number.

During the 1960's, the successful development of modern GLC (gas liquid chromatography) permitted the accurate determination of the individual fatty acids in a reasonable time. Because of this, it is now more acceptable to quote analyses for individual fatty acids, particularly the unsaturated oleic, linoleic and linolenic acids. Since all of the measurements listed are currently in use and will always be used, it is desirable to have all the values for a given oil sample.

A number of workers (Pickering and Cowlishaw, 1922; Cheneveau, 1925; Geddes, 1935; Majors and Milner, 1935; Joglekar and Jatkar, 1939; Haydon, 1969) have found relationships between refractive index (n) and iodine value (I.V.) of various oils (linseed, soybean, cottonseed, peanut, safflower and sunflower). Hunt *et al.*, (1951) designed a refractometer calibrated directly in iodine number units for testing flaxseed and soybean oils.

The iodine value is defined as the number of grams of iodine that will combine with one hundred grams of oil. It is a direct chemical measurement of the degree of unsaturation.

The refractive index of a substance is a physical property which can be related to structure. The main structural difference in vegetable oils is the number of double bonds in the fatty acids of the triglycerides. Additional double bonds, and particularly conjugated double bonds, increase the refractive index. Refractive index varies with density which is dependent on temperature. Wright (1919) and Joseph (1920) have investigated the change of refractive indices of oils with temperature. Temperature must be controlled and carefully specified for accurate refractive index measurements.

Rau and Roseveare (1936) designed a differential refractometer with some advantages over the conventional instrument. With the reference and sample cells in temperature equilibrium the instrument was less sensitive to temperature changes. Also, by making differential measurements, resolution was improved. Instrument companies have, in recent years, developed the differential refractometer for use as a liquid chromatography detector.

Sunflower oil consists mainly of triglycerides apart from minor percentages of waxes, phospholipids and high molecular weight hydrocarbons. Because the sum of the unsaturated acids, oleic and linoleic acids, is approximately constant the iodine value is related to the proportion of oleic and linoleic acids. Simpson (1977), Goss (1978), and Ermakov and Popova (1975) have taken this further, relating oleic and linoleic acid contents to the measured refractive index.

The relations apply strictly only to the freshly pressed oil. If there is oxidation and polymerisation during storage, the refractive index rises and calculated percentages of linoleic and oleic acids will lose their accuracy. Also, additives in or refinement of commercial oils could cause errors in the calculations. Goss (1978) has stated that extracted oils gave inconsistent refractive index measurements as compared with measurements on pressed oils. Presumably, this is because extraction produces an oil with a larger nontriglyceride component or because of the difficulty of removing solvent traces from the extracted oil.

Following the rapid expansion of the sunflower industry in Australia, Simpson (1977) used the refractive index technique to produce a rapid method of obtaining the iodine value, linoleic and oleic acid levels in a sunflower oil at any known temperature. The method involved measurement of the refractive index of the oil and the exact temperature of the oil. Linear equations were then used to calculate iodine value and percents oleic and linoleic acids. Operational difficulties arose from using the refractometer (Abbe instrument) at its very limit of resolution and consistently having to measure the temperature to an accuracy of 0.1°C.

The next logical step in the process was to build the measuring and calculating functions into the one instrument. This has now been accomplished. This paper describes the principle of operation, construction and preliminary testing of the instrument.

MATERIALS AND METHODS

Principle of Operation

The Oil Quality Analyser uses a differential refractometer to measure the difference in refractive index between a reference sunflower oil and the oil under test. This difference expressed as an analogue voltage is amplified, converted to a digital form by an analogue to digital converter and passed to a microprocessor system. The microprocessor calculates values for the refractive index, iodine value and percents linoleic and oleic acids and controls the display of these values on digital counters.

A differential refractometer was expected to be much less susceptible to temperature effects than a normal refractometer. If the reference and sample cells of a differential refractometer are in temperature equilibrium, and if the reference and sample materials have very similar expansion coefficients, then the change in the difference of refractive indices should be much less than the absolute change caused by a temperature fluctuation.

Also resolution of a differential refractometer is specified as being better than the conventional Abbe refractometer. These two characteristics, the reduced effect of temperature and the increased resolution, made the differential refractometer the choice for the measuring instrument.

To retain constants to be used in the calculations, to make the calculations and to display the results, the instrument uses a microprocessor system. A microprocessor also has the advantage of flexibility; constants can readily be changed by keyboard entry. The microprocessor can also carry out digital filtering of a noisy signal to help produce a steady meaningful output.

The analogue voltage from the differential refractometer must be converted to a digital form for acceptance by the microprocessor. An analogue to digital converter using a successive approximation register produces an output which is a 12-bit binary number.

Display of results is achieved by passing the correct number of pulses from the micro-processor to digital counters and displays.

In use, a reference oil of known % linoleic acid is introduced into both cells and the instrument is set to read this % linoleic acid. Samples of oil (volume 1 ml) are then introduced into the sample cell and the values for iodine value, refractive index and % linoleic and oleic acids may be read from the displays after 1 to 2 minutes.

Instrument Hardware — Mechanical

The instrument frame was constructed from 25 x 25 x 3 mm angle aluminium using welded joints throughout. The display, control and back panels were made from anodised aluminium (1.6 mm), and the outer panels from 'Marviplate' (plastic coated steel).

End panels were designed for easy removal to allow for servicing. A hinged panel on the top-front surface was incorporated to protect the control knobs from accidental bumping or oil spillage during operation. The microprocessor keyboard (not required under normal operating conditions) was also housed under the hinged panel.

A Waters Model R-404 Differential refractometer was modified to accommodate the viscous oil samples. Both inlet and outlet tubing were significantly reduced in length. Stainless steel Luer fittings were silver soldered to the inlet tubing to enable injection of the oil using either Luer or Luer-Lok syringes.

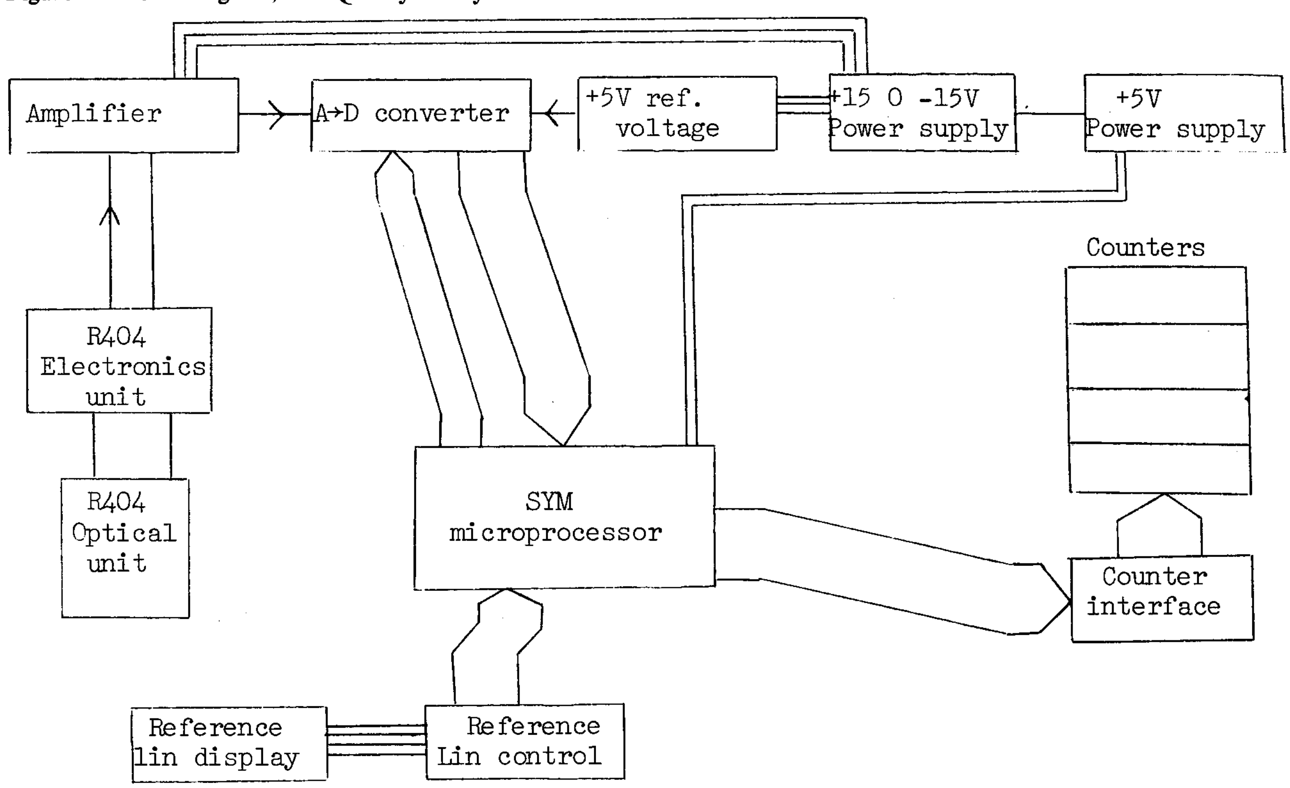
The shortened stainless steel outlet tubing is connected to larger I.D. teflon tubing to reduce backpressure and to provide a sink which helps to prevent oil flow through the cells on standing. The outlet of this tubing terminates in a specially designed cup which has an adjustable height to ensure that both inlet and outlet ports are at exactly the same level.

It is essential for correct operation of the Oil Quality Analyser that the sample remains stationary in the cell. Temperature equilibrium must be reached as soon as possible after injection. This can not be obtained when the sample is moving.

Instrument Hardware — Electronic

The general scheme of hardware connections is shown in the block diagram of Fig. 1. The heart of the system is the Synertek SYM-1, which uses the 6502, and 8-bit microprocessor.

Figure 1. Block diagram, Oil Quality Analyser.



The SYM-1 is programmed to accept a value for the linoleic acid percent of the reference oil, begin the A→D converter cycle, receive the output of the A→D converter, make the calculations required and control the operation of digital counters to display the results.

A regulated 5V (2A) power supply was constructed to power the microprocessor and digital displays. A separate ± 15V power supply was required for the operation amplifiers used in the amplifier and reference voltage circuits.

The A→D converter using an ADC1210 required a reference voltage to act as a full scale for the conversion. The ADC1210 is a low power, medium speed, 12-bit successive approximation analogue-to-digital (A→D) converter. It requires a reference voltage and a clock for its operation, but within the ADC1210 are the successive approximation logic, CMOS analogue switches, R-2R ladder network and FET input comparator. The device offers 12-bit resolution and 12-bit accuracy.

Microprocessor operation

The operational program, stored on EPROM, is designed to start automatically from switch-on and then to continue in a cyclic manner so as to continually update the sample input. This repetitive sampling leads to more convenient operation and enables new samples to be tested without any further program starting by the operator.

The calculation of percent linoleic acid, percent oleic acid and iodine value from a refractive index measurement was based on the work of Simpson. The equations (using the refractive index measured at 25°C) are as follows —

% Linoleic Acid $= 11665\ n_D\ (25°C) - 17116.3$ —1

% Oleic Acid $= -12562.2\ n_D\ (25°C) + 18526.6$ —2

Iodine Value $= 9824.4\ n_D\ (25°C) - 14339.5$ —3

The percent linoleic acid of the reference oil must be known. This value is entered into the instrument so that it can be used as a reference point for all further samples. From this value, the program calculates reference values for oleic acid, iodine value and refractive index.

Differences in refractive index between sample and reference oils are output from the differential refractometer as analogue voltages, amplified, and converted to digital (A→D converter) form. All equations used in the microprocessor program have been suitably modified to accommodate the concept of a 12-bit number representing refractive index difference and also to be compatible with machine code programming.

RESULTS AND DISCUSSION

Initial testing of the instrument involved determining the optimum sample size required. Oils A and B were alternately injected each 10 times. Values were read at 30 sec, 1 min and 2 min after sample injection. The mean and standard deviation for the 10 readings were calculated for each of the three times. This test was performed for sample volumes of 0.5, 1.0, 2.0 and 3.0 ml. The results demonstrated that 1.0 ml samples were sufficient to wash out the previous sample and provide a meaningful result and that readings could be reliably taken 1 — 2 minutes after injection. The standard deviation for % linoleic acid, % oleic acid and iodine value was in the range 1 — 1.5 units and for refractive index was 0.00008 — 0.00013.

In a practical situation, where sufficient sample is available, an additional 1.0 ml sample should be injected and the mean of the two sets of results taken. When successive ten 1.0 ml injections of either sample A or B were tested for reproducibility, the standard deviation was reduced to 0.3 for % linoleic acid, % oleic acid and iodine value and 0.00004 for refractive index.

The day to day variation in results was tested by reading samples each day for 6 days. The variation was no more than for samples read on the same day. These results demonstrated the consistency of the instrument.

Table 1 compares results from the Oil Quality Analyser (OQA) with refractive index values (25°C) measured by Abbe refractometer, GLC fatty acid analysis and chemically determined iodine value.

Table 1. Comparison of results obtained by different methods.

Sample	Date of pressing	Method	Date of analysis	Linoleic acid %	Oleic acid %	Iodine value	Refractive index
124	31.8.81	OQA	Sept. 81	65.8	23.1	131	1.4729
		Abbe	Sept. 81	—	—	—	1.4729
		GLC	Sept. 81	64.6	24.1	—	—
		Chemical	Sept. 81	—	—	130	—
998	31.8.81	OQA	Sept. 81	73.9	14.3	138	1.4736
		Abbe	Sept. 81	—	—	—	1.4739
		GLC	Sept. 81	73.1	15.8	—	—
		Chemical	Sept. 81	—	—	135	—
1004	31.8.81	OQA	Sept. 81	74.4	13.7	139	1.4737
		Abbe	Sept. 81	—	—	—	1.4739
		GLC	Sept. 81	72.3	16.5	—	—
		Chemical	Sept. 81	—	—	136	—

At the time of writing this paper, insufficient samples had been analysed on the instrument for extensive comparison studies. Before the instrument can be finally calibrated, a large number of samples covering the full physiological range must be analysed by the Oil Quality Analyser and traditional techniques. Following statistical analysis of the results obtained some minor adjustment may be required. Provision has been made in both the electronic design and the microprocessor program for any such adjustments if found to be necessary.

CONCLUSION

The objective of this work was to develop an instrument that would automatically measure the refractive index of a sunflower seed oil and give an instant reading of refractive index, iodine value, and percents linoleic and oleic acids displayed on digital readouts. This objective has been achieved with the development of a fully working prototype.

ACKNOWLEDGEMENT

The authors wish to acknowledge the support of the Oilseeds Research Committee who funded this project for the year 1980 — 81.

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