SULPHUR IN RAPESEED OIL

by

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ABSTRACT

Several methods for the determination of sulphur in rapeseed oil were examined. In the preferred method a sample is heated with Raney nickel. Nickel sulphide, formed by reduction of sulphur compounds, is digested in strong acid. The hydrogen sulphide which is released is absorbed in caustic solution and titrated with mercuric acetate using dithizone as an indicator. For a 20-g sample of oil, the useful range is 1-50 ppm sulphur. The detection limit is about 0.5 ppm. The precision (2σ) is about $\pm$ 10% above the 10 ppm level and $\pm$ 1 ppm below the 10 ppm level.

The sulphur content of samples of oil from various industrial processing steps was determined using the above method. The sulphur content of expelled oils was fairly constant, about 20 ppm, but the sulphur in the extracted oils varied widely, from 10 to 50 ppm, apparently depending on the amount of gum and dark coloured material present in the oils. The sulphur content of degummed, refined, and bleached oils was approximately proportional to the sulphur content of the crude oils. Deodorization of refined and bleached oils lowered the sulphur content to about 1 ppm, while hydrogenation lowered the sulphur content of refined oils to about 1 ppm. Most of the sulphur was found on the nickel catalyst after hydrogenation.

Laboratory extraction studies showed that it was possible to

extract sulphur-free oil from seeds which were not heated to destroy enzyme activity, even if the seeds were crushed long before extraction. Excessive heating, increased moisture, frost damage, or greenness of the seeds resulted in increased sulphur in the oil. Under similar conditions less sulphur was extracted into the oil from low glucosinolate seeds than from high glucosinolate seeds.

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1. INTRODUCTION

About 50 naturally occurring glucosinolates have been found, mostly in plants of the Cruciferae family. Some glucosinolates found in rapeseeds are shown in Table 1. When rapeseed is damaged - i.e., by crushing - enzymes are released which catalyze the hydrolysis of glucosinolates to form isothiocyanates and thiooxazolidones (Fig. 1 and 2). These compounds have goitrogenic properties and their presence in rapeseed meal has hampered its utilization as a protein supplement in animal feed. Methods for treating rapeseed meal to remove glucosinolates have been described but generally these are not economical or they also remove desirable portions of the meal. Plant breeders are attempting to develop glucosinolate-free varieties of rapeseed.

Difficulties in hydrogenating rapeseed oil is a further problem which may also be associated with glucosinolates. These difficulties have been ascribed to the presence of isothiocyanates in the oil. Isothiocyanates contain sulphur which might poison the catalyst used in the hydrogenation process. There have also been some undocumented reports linking off-flavours of rapeseed oil with sulphur compounds. Although these concepts have been expressed for some time, little information is available on the occurrence of sulphur in rapeseed oil. Also, a simple and reliable method for the determination of sulphur in rapeseed oils has not been available. Such a method could possibly aid in quality control during the processing of rapeseed oil. Information on the quantities of sulphur present in the oil at different industrial processing

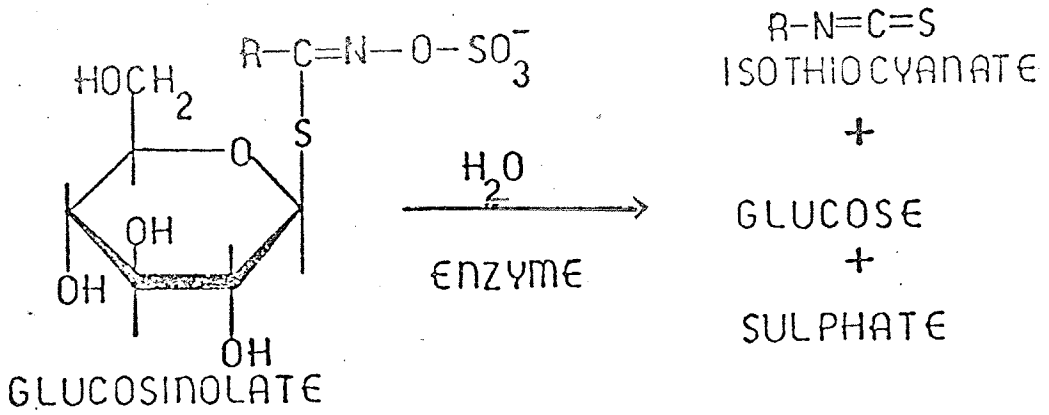
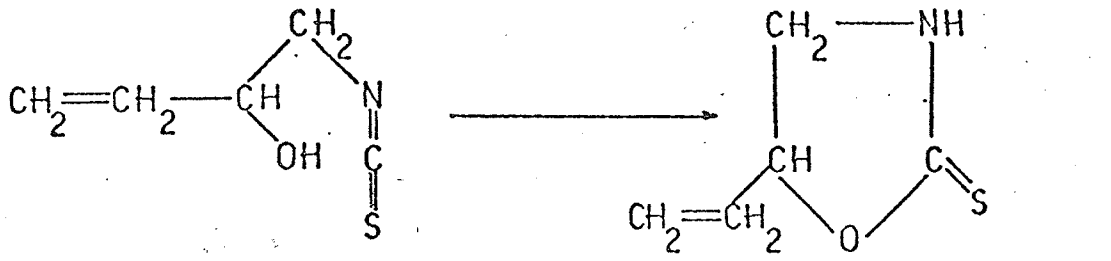


FIG.1 ENZYMATIC HYDROLYSIS OF GLUCOSINOLATES



2-HYDROXY-3-BUTENYL ISOTHIOCYANATE

5-VINYL-2-THIOOXAZOLIDONE

FIG. 2 FORMATION OF 5-VINYL-2-THIOOXAZOLIDONE

TABLE 1

Some glucosinolates found in rapeseed

Name	Concentration* (mg glucosinolate/g seed)	
	B. napus	B. campestris
3-Butenyl glucosinolate	3 - 5	3 - 5
R-2-Hydroxy-3-butenyl glucosinolate	15 - 20	4 - 6
4-Pentenyl glucosinolate	1	3 - 7
4-Methythiobutyl glucosinolate		trace
5-Methylthiopentyl glucosinolate		trace
2-Phenylethyl glucosinolate	trace	trace

* Based on analyses by B. G. Olafson

stages would also be of interest to processors.

The objectives of this study were (a) to find a simple method for the measurement of small quantities of sulphur in rapeseed oil, (b) to determine the effects of industrial extraction and refining on the sulphur content of rapeseed oil, (c) to determine the effects of hydrogenation on the sulphur content of rapeseed oil, and (d) to study some extraction and seed conditions which may influence the quantities of sulphur obtained in rapeseed oil.

Before presenting the experimental work relating to the above objectives, it was considered useful to review the literature related to the problems as well as to define the terms which are used in this study. Thus, the next two chapters present a discussion of the processing of rapeseed oil and a review on the occurrence and determination of sulphur in rapeseed oil.

II. PROCESSING OF RAPESEED OIL

Outline of processing steps

Rapeseed oil must first be removed from the rapeseeds by crushing and extraction. Besides triglycerides, the oil may contain free fatty acids, phospholipids, sterols, carotenoids, chlorophylls, resins, protein fragments, carbohydrates, and mucilagenous substances. Many of these substances are undesirable as they are associated with bad oil flavours and may hinder certain oil treatments such as hydrogenation. A series of processing steps have been designed to remove such undesirable impurities and to produce an oil with properties acceptable to the consumer. The processing steps, as outlined below, are usually carried out in the order given. Degumming is sometimes omitted and bleaching may be carried out before refining. Oils are hydrogenated only to produce products such as shortening and margarine. There is no standardized terminology in commercial oil processing but the most commonly used terms are those used in this study. A comprehensive discussion of oilseed processing is given in "Bailey's" treatise on fats and oils (60).

Cooking. The seed is initially cleaned to remove foreign material. Large seeds are also dehulled or cracked but

this is usually not feasible for small seeds such as rapeseed. After cleaning, rapeseed is usually heated for up to 30 minutes at temperatures up to 100° C to inactivate enzymes and to adjust the moisture content of the seeds for maximum oil recovery.

Expelling. Cooked seeds are sent through a continuous crushing and flaking operation which removes about 70% of the oil from the seeds. The flake size is adjusted to give maximum efficiency of the subsequent extraction while avoiding excessive fragility of the flakes.

Extraction. After expelling, the residual meal is extracted with a hexane-type solvent to remove the remainder of the oil. The solvent is removed from the extracted oil by distillation.

Crude oil. Crude oil usually refers to the combined expelled and extracted oils.

Degumming. The oil is mixed with water to hydrate phospholipids and other polar material, thus making them insoluble in the oil. The hydrated material is removed by centrifugation.

Refining. Degumming does not remove free fatty acids from the oil. Free fatty acids are most commonly removed by "alkali refining," that is, neutralization of the free fatty acids by a slight excess of alkali and removal of the

insoluble soaps by centrifugation or filtration. Caustic soda is the alkali most frequently employed, but soda ash, sodium bicarbonate, and ammonium hydroxide have also been used. Alkali refining also removes phospholipids and some of the other undesirable components. Rapeseed and linseed oils may be acid refined instead of alkali refined in order to remove phosphatides and gum material. Free fatty acids are not removed by acid refining.

Bleaching. The oils are mixed with bleaching clays (activated earths) in order to remove chlorophyll and carotenoid pigments. Bleaching is also effective in removing phospholipids and other mucilagenous materials.

Hydrogenation. The refined and bleached oil is treated with hydrogen in the presence of a catalyst, usually nickel, to produce a more saturated oil which has a higher melting point and is more stable to oxidation. Besides promoting the hydrogenation reaction, nickel catalyzes the cis-trans isomerization of double bonds within the fatty acid chains. This isomerization is important to processors since trans isomers have a higher melting point than the corresponding cis forms. Only the naturally occurring all-cis forms of linoleic, linolenic, and arachidonic acid, however, are considered biologically active as essential fatty acids.

Depending on the operating conditions and the nature of the catalyst, hydrogenation may proceed more or less sel-

ectively. Non-selective hydrogenation involves a random hydrogenation of the fatty acids while selective hydrogenation involves hydrogenation of the fatty acids in a certain order; usually the most unsaturated fatty acid chains are hydrogenated first. Most hydrogenations, however, are only partially selective. In general, selective hydrogenation takes place at low hydrogen pressures and low catalyst activity. It is usually accompanied by pronounced cis-trans isomerization.

Deodorization. Refined and bleached oils often have unpleasant flavours while hydrogenated oils often develop "hydrogenation off-flavours" which make these oils extremely unpalatable. The compounds responsible for these flavours are generally of low molecular weight and are relatively volatile. Deodorization involves removal of these compounds by distillation, usually with steam in a partial vacuum. Low molecular weight flavour compounds such as short-chain aldehydes and fatty acids are easily removed by deodorization. Higher molecular weight flavour compounds, such as those produced by breakdown of erucic acid, are not as readily removed.

Problems in processing of rapeseed oil

Most problems encountered in the processing of rapeseed oil can be related to seed quality or to extraction conditions. Some problems in hydrogenation are due to the pre-

sence in the oil of catalyst poisons, possibly including sulphur.

Seed quality. It has been reported that rapeseed oil from seed which had been attacked by mould and bacteria was dark, had an offensive odour, and contained relatively large quantities of nitrogen and sulphur compounds. Although conventional refining methods removed the sulphur compounds, the nitrogen compounds and offensive odour remained. Acid refining was found to be most efficient in removing all these undesirable compounds (17). Oil from mouldy rapeseeds has also been found difficult to hydrogenate. The difficulty was directly related to the degree of mould growth and may have been due to increased amounts of phosphorus in the oil (6). Mouldy seed has also been reported to have poor storage stability, and to contain less oil and more moisture than healthy seeds. The oil from mouldy seeds also may contain more free fatty acids and have a lower iodine value than the oil from healthy seeds (55).

Large, mature rapeseed with moisture content less than 9% has been reported to store well and to give a good quality oil (43). Seed stored at 40° C may give oil with high acidity and low stability. Storage at 2-20° C is recommended but freezing is deleterious to the oil quality (30).

The phospholipid and sterol content of rapeseed oil has been found to depend on the original moisture content of the seed

(33); oil from seed with high moisture content would thus contain relatively large amounts of polar lipids which could increase the refining cost.

Extraction conditions. There have been several studies on processing conditions which would allow maximum oil extraction efficiency, deactivate enzymes, and produce a good quality oil. Rapeseed dried with flue gases down a temperature gradient from 120° C to 60° C produced an oil with free fatty acid content and organoleptic qualities similar to oil from fresh seeds. Enzymes were inactivated and peroxide values varied irregularly (29). Dry heating of crushed seed at temperatures close to but not exceeding 100° C inactivated enzymes and produced a satisfactory oil (54). Soaking seeds in boiling water resulted in enzyme inactivation and produced a better oil colour than dry heat, steam blanching or microwave heating (20).

Most commercial extraction procedures are designed to remove the oil from the meal as completely as possible. The last portions of oil removed from the meal, however, may contain large amounts of phospholipids and nonsaponifiable materials. Refining losses of the last 1% of material extracted may be as high as 80% (50). In view of the difficulty and expense involved in removal of the above materials from the oil it may be worthwhile for processors to consider using a slightly lower efficiency of extraction in order to

improve the quality of the oil extracted.

Hydrogenation. Difficulty in the hydrogenation of rapeseed oil has been ascribed to the presence of peroxides (13), to calcium, magnesium and iron soaps (21), and more recently to sulphur (48, 63). Erucic acid has even been implicated in inhibiting the hydrogenation of "sulphur-free" rapeseed oil (67). Recently, a Canadian processor has noted some difficulties in hydrogenating the newly produced "Low-Erucic-Acid Rapeseed Oil (LEAR oil)". They feel that sulphur may be a cause of this difficulty (personal communication, G. Davidson, Canada Packers, Winnipeg).

The influence of different catalysts on the geometrical isomerization of rapeseed oil has been studied (31). When used catalyst was substituted for fresh catalyst the rate of isomerization increased by a factor of eight relative to the rate of hydrogenation. Sulphur-deactivated catalysts produced similar results (10).

A study of the relative influence of different sulphur and phosphorus compounds in poisoning the hydrogenation of rapeseed oil indicated that the amino acids cysteine and methionine were required to be present in the oil in concentrations considerably greater than 2.5 ppm sulphur to cause a significant effect while allyl isothiocyanate or 5-vinyl-2-thiooxazolidone caused a 50% reduction in the rate of hydrogenation at a 2.5-

ppm level of sulphur in the oil. Lecithin phosphorus, when present in the oil at a 5-ppm level, caused a distinct deactivation of the catalyst (7).

Molecular distillation may be a possible means for producing an oil free from sulphur, phosphorus and heavy metals as hydrogenation inhibitors (49). Preliminary hydrogenation has been shown to remove the catalyst inhibitors from sulphur-containing oils (47). Even bleaching with used catalyst has been shown to be effective in removing sulphur from oils prior to hydrogenation (51).

Catalyst poisoning

The basic reaction of catalytic hydrogenation is indicated in Figure 3. The critical function of a catalyst is the bringing together of the reactants in such a way that the activation energy is lowered. The nature of the catalyst surface is most important. All theories of catalyst action assume the presence of a few highly reactive catalyst atoms, "active sites", on the surface of the catalyst (Figure 4). Catalytic action may be poisoned or hindered by an irreversible reaction of the active sites with some reactive contaminant present in the substrate. Since catalysts are usually present in very low concentrations, they may be poisoned by very small quantities of reactive contaminants.

Sulphur compounds are among the most active poisons for

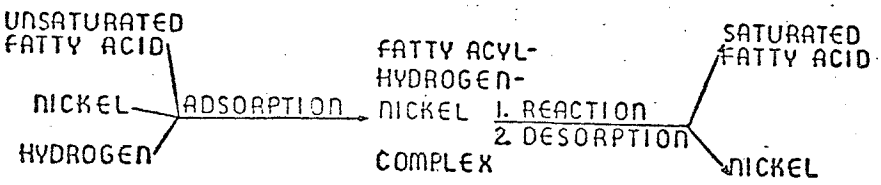


FIGURE 3 CATALYTIC HYDROGENATION OF FATTY ACIDS.

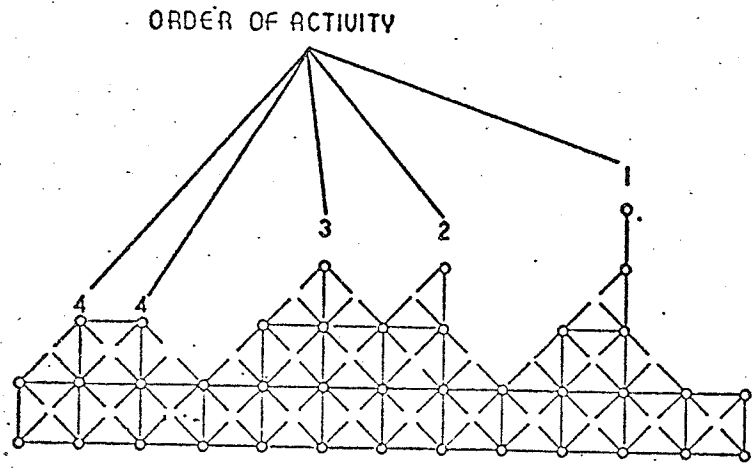


FIG.4 SCHEMATIC REPRESENTATION OF A CATALYST SURFACE.

nickel hydrogenation catalysts. Depending on their original activity, nickel catalysts may be completely poisoned by amounts of sulphur ranging from 0.5 to 5% of the catalyst weight (44). The degree of poisoning depends on the number of active sites available and on the molecular size of the sulphur compound (5, p.189). For very active catalysts, however, more sulphur than expected is tolerated before complete deactivation occurs (44). The type of sulphur compound involved is also important. For example, the isothiocyanate compounds from rapeseed have been found, as earlier indicated, to be much more active inhibitors of rapeseed oil hydrogenation than the sulphur amino acids (7).

Effect of oil processing on minor constituents

Oil processing is carried out in order to remove undesirable components from the oil and to produce a palatable and stable product. Some desirable components such as tocopherols and carotenoids are also removed to a certain extent during processing. The effect of processing on various components is summarized in Table 2.

Free fatty acids are almost completely removed by refining. Bleaching and hydrogenation, however, often cause slight increases in the free fatty acid content of refined oil but deodorization usually lowers the free fatty acid content again to more acceptable levels. Phosphorus and nitrogen com-

TABLE 2

Contents of minor constituents in processed rapeseed oils

Constituent	Content in oil					
	Crude	Degummed	Refined	Bleached	Hydrogenated	Deodorized
Free fatty acids (%)[a]	1.5	1.5	0.02	0.06	0.2	0.03
Phosphorus (ppm)[a]	1000	30	0.5			
Nitrogen (ppm)[a]	200	3	1			
Chlorophyll (ppm)[b]	1.0		1.0	0.02		
Tocopherols (ppm)[c]	580	430	200			
Copper (ppm)[d]	1.5		0.8			0.01
Iron (ppm)[d]	20		10			0.3
Zinc (ppm)[d]	36		1	0.1		
Nickel (ppm)[d]	10		7	0.1	1	

a. References 44, 50, 51.

b. Reference 51.

c. Reference 56.

d. References 32, 44, 61, 62, 64, 72.

pounds are almost completely removed by degumming or bleaching. Bleaching also effectively removes chlorophyll, carotenoid compounds and metallic elements. Tocopherols may be substantially removed during processing.

III. OCCURRENCE AND DETERMINATION OF SULPHUR

Occurrence of sulphur in rapeseed oil

Aside from some undocumented references in reviews, there have been no reports in the recent literature on the occurrence of sulphur in rapeseed oils. Such reports as do exist come from the period 1945 to 1957 when the techniques for refining rapeseed oil and for determining sulphur had not reached their present degree of sophistication. It is not to be expected, therefore, that results from these studies always should be in agreement with present-day results.

Von Fellenberg (22) analysed samples of expelled, solvent extracted, and refined oils. He reported sulphur contents of 25, 31, and 13 ppm, respectively (Table 3). He also noted that all the sulphur was contained in the sediment of the expelled and the solvent extracted oils.

Andre (2) showed oil from *B. napus* variety *oleifera* to contain about 100 ppm sulphur. He later reported that the nonsaponifiable portion of the oil contained 1600-2000 ppm sulphur (3). On the other hand, Lips (40) indicated that the sulphur content of erucic-acid-containing oils was less than 10 ppm.

TABLE 3

Various reports on the sulphur content (ppm) of commercially processed oils

Study	Expelled	Extracted	Crude	Refined	Bleached	Deodorized
von Fellenberg[a]	25	31		13		
Kucera and Hejtmanek[b]			500	50	250	5
Zeman and Zemanova[c]	40	600				

[a] Reference 22.

[b] Oil was bleached before refining, reference 37.

[c] Calculated from results for isothiocyanates and thiooxazolidones, Reference 73.

Kucera and Hejtmanek (37) found the sulphur content of crude rapeseed oil to be 400-500 ppm. This decreased to about 250 ppm on bleaching, to 50 ppm on refining, and to about 5 ppm on deodorization (Table 3).

Zeman and Zemanova (73) studied the effect of processing on the content of isothiocyanates and 5-vinyl-2-thiooxazolidone in rapeseed meal and oil. According to their results, expelled oil contained 25-50 ppm sulphur while extracted oil contained 450-1100 ppm sulphur (Table 3).

Determination of sulphur in petroleum oils

Generally, the petroleum industry has provided the incentive for the determination of small amounts of sulphur in liquid organic materials. The area has been reviewed recently (41, 45, 46). A description of the general methods and their limitations follows.

Oxidative methods A summary of oxidative methods is presented in Table 4. Originally, samples were oxidized by burning in a lamp followed by absorption of the sulphur oxides in water and their determination by titration, colourimetry, or turbidimetry. Adaptations involved the introduction of combustion burners (Wickbold burners) and tube furnaces (oxydative pyrolysis). The Schöniger flask combustion method is usually not used because of difficulties in sample size and handling. Oxidative methods are quite useful for relatively high sulphur concentrations. To determine low levels of sul-

TABLE 4

Oxidative methods for determination of sulphur in petroleum oils

Method of oxidation	Method of sulphur determination	Detection limit (ppm)	Reference
Lamp methods	Iodometry	10,000	14
	Microcoulometry	200	14
	Chelatometry	1	57
	Conductivity	100	26
	Radiometry	1	24
	Nephelometry	1	26
Wickbold burner	Oscillometry	100	42
	Chelatometry	0.1	57
	Nephelometry	0.1	39
	Titrimetry	0.1	69
Oxidative pyrolysis	Microcoulometry	0.1	19, 68
	Colourimetry	1	16
	Gas chromatography	1000	71
Flask combustion	Colourimetry	200	38

TABLE 5

Reductive methods for determination of sulphur in petroleum oils

Method of reduction	Method of sulphur determination	Detection limit (ppm)	Reference
Raney nickel	Titration	0.01	23, 25
	Polarography	20	65
	Colourimetry	0.05	11
Reductive pyrolysis	Microcoulometry	2	68
Potassium	Titration	0.5	36
Mercury or copper	Isotope dilution	0.3	27
Catalytic hydrogenation	Titration	25	58

phur, however, large samples must be burned to produce sufficient sulphate for determination. Often, samples also must be treated to remove elements which interfere with sulphate determination. The limit of detection is about 0.1 ppm with relative errors from 5 to 50% (35).

Reductive methods. An outline of reductive methods is presented in Table 5. These methods usually rely on reductive pyrolysis or desulphurization with an active metal. Hydrogen sulphide formed on reduction is usually trapped in caustic solution or a solution of a metal ion which forms an insoluble sulphide. The sulphide ion may be determined colourimetrically or by titration, usually with a mercury salt. The reductive methods have the advantage of being specific, sensitive, and relatively free from interference. Sulphur oxides, however, are usually not reduced (70). Detection limits as low as 0.01 ppm have been reported, although 0.5 ppm is a more generally attained limit. Relative errors of 3-10% have been reported (35).

Spectrometric methods. Sulphur may be determined by atomic absorption spectroscopy in concentrations as low as 10 ppm (34) and by flame photometry in concentrations as low as 0.08 ppm (1). Application of these methods depends largely on the sample being easily atomized and burned; these methods are thus not readily applicable to many organic materials.

X-ray fluorescence has been used for the detection of as little as 1 ppm sulphur (15, 28), while X-ray and γ-ray absorption are routinely used for the on-line determination of 0.05-2% sulphur in petroleum processing (18, 59). Neutron activation analysis has been used for the determination of sulphur at the 0.1% level in gasoline (53).

Determination of sulphur in glyceride oils

There have been few published methods specifically for the determination of sulphur in glyceride oils, probably because of the ready applicability of the above petroleum methods for this purpose.

Industrial processors claim that sulphur concentrations in excess of 3-7 ppm in refined oils cause significant retardation of the hydrogenation process (B. Weinberg, unpublished report). A method for determination of sulphur should thus be capable of detecting about 1 ppm sulphur in rapeseed oil. The method should also be applicable for a wide range of concentrations and should be simple and readily adaptable to quality control analysis.

André and Kogane-Charles (4) reported a method which involved a complicated ignition with MgO and Na_2CO_3 followed by dissolution in water and oxidation with bromine. Sulphate was determined by turbidimetry as $BaSO_4$. Precision, accuracy, and sensitivity were not reported.

Lips (40) of the National Research Council, Ottawa, reported that standard methods of sulphur analysis were unsatisfactory for the analysis of oils with high erucic acid content. He recommended a preliminary overnight oxidation with 90% H_2O_2 followed by ignition with NaOH and turbidimetric determination of sulphur as sulphate. He was able to determine a lower limit of about 10 ppm sulphur in rapeseed oil.

Pippen and Mecchi (52) reported a method for the estimation of less than 10 ppm sulphur in poultry fat. Samples were oxidized at 1000° C on a vanadium oxide catalyst. Sulphur oxides formed were converted to sulphate and the sulphate reduced to H_2S. The H_2S was determined by the formation of methylene blue. They were able to distinguish between samples differing by 0.5 ppm sulphur. Recoveries were 73-90% at the 0.5-2 ppm level of sulphur.

Kucera and Hejtmanek (37) determined the sulphur content of rapeseed oil by reduction of the sulphur compounds with nascent hydrogen produced in the reaction of aluminum with HCl. The H_2S formed was determined by the darkening of lead acetate strips. They were able to detect 0.3 ppm sulphur with an error of ± 20%.

Baltes (9) determined 0.5-100 ppm sulphur in whale and fish oils by Raney nickel reduction. The H_2S formed was trapped in caustic solution and determined by titration with mer-

curic acetate using a dithizone indicator. He recommended the method also for the determination of sulphur in rapeseed oil. Babuchowski and Zadernowski (8) reported the determination of 0.9-100 µg sulphur in rapeseed oil using a similar method.

IV. EXPERIMENTAL

Flask combustion method

A 100-mg sample of oil was burned in a Schöniger oxygen flask. Sulphur was oxidized to a mixture of SO_2 and SO_3 which was absorbed in a dilute solution of hydrogen peroxide to form sulphate ion. Sulphate ion was determined turbidimetrically with barium chloride or colourimetrically with barium chloranilate (12).

Tube combustion method

In accordance with Pippen and Mecchi (52), 10 g of oil was oxidized by passing it through a Vycor tube containing a vanadium oxide catalyst at 1000° C. Sulphur oxides formed were trapped in a dilute solution of hydrogen peroxide where they were oxidized to sulphate. The solution was evaporated to dryness and sulphate was converted to sulphide by reduction with periodic acid. Hydrogen sulphide evolved was trapped in zinc acetate solution and sulphide was determined colourimetrically by formation of methylene blue.

Raney nickel reduction method

Reagents.

1) 2.5 N NaOH: 100 g A.C.S.-grade NaOH was dissolved

in one liter of distilled water.

2) 1.0 N NaOH: 40 g A.C.S.-grade NaOH was dissolved in one liter of distilled water.

3) 60% HCl: 600 ml C.P.-reagent HCl was added to 400 ml of distilled water.

4) 2-Propanol/5% H_2O: 50 ml of distilled water was diluted to one liter with A.C.S.-grade 2-propanol.

5) Raney nickel: Raney nickel was prepared from nickel-aluminum alloy as described below.

6) Dithizone indicator: 10 mg A.C.S.-grade diphenylthiocarbazone (dithizone) was dissolved in 50 ml acetone.

7) Permanganate scrubbing solution: 4 g $KMnO_4$ and 14 g $HgCl_2$ were dissolved in 200 ml H_2O.

8) Nitrogen: water-pumped grade nitrogen was used. The gas was passed through a gas-scrubbing apparatus to remove sulphur.

9) Mercuric acetate titrant: 10.0 g of A.C.S.-grade mercuric acetate was dissolved in a solution of 32 ml glacial acetic acid in 100 ml H_2O. The resulting solution was diluted to one liter with distilled water. The titrant was standardized by titrating aliquots with standard 0.05 N KCNS with a ferric alum indicator. One milliliter mercuric acetate titrant equaled approximately one milligram of sulphur as sulphide.

Equipment.

1) Reduction apparatus as shown (Figure 5).
2) Water bath thermostated to 50° C.
3) Centrifuge with 50-ml centrifuge tubes.
4) 2.000-ml micrometer burette.
5) Magnetic stirrer with teflon-coated stirring bar.
6) Heating mantle for reduction flask, equipped with variable transformer.
7) Gas-scrubbing apparatus: before being introduced into the reduction flask, the nitrogen was passed through two gas-scrubbing bottles, the first filled with permanganate scrubbing solution and the second with distilled water.
8) Nitrogen flow regulator: since a low-pressure regulator (0-30 psi) was used, a needle valve was found to provide adequate regulation of the nitrogen flow.

Preparation of catalyst. Approximately 2 g of nickel aluminum alloy was placed into a 125-ml Erlenmeyer flask. This amount was sufficient for two determinations, each requiring 500 mg of activated catalyst. About 5 ml water was added to the flask and the flask was placed in an ice bath in a fume hood and was allowed to cool for 10 min. After cooling, 30 ml of 2.5 N NaOH was added to the flask and the contents were mixed.

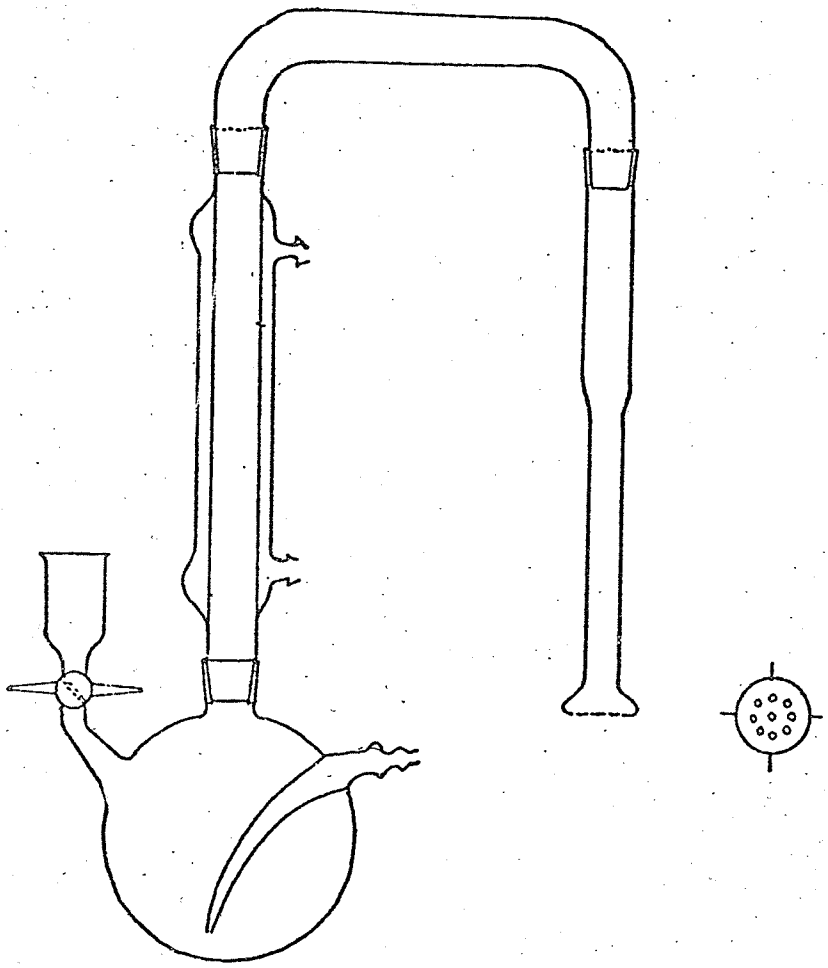


FIGURE 5. RANEY NICKEL REDUCTION APPARATUS

The flask contents were allowed to react for 30 min after which the flask was transferred to the 50° C water bath for about 3 hr. The slurry was then divided into two equal portions and transferred to two 50-ml centrifuge tubes. The tubes were centrifuged at low speed to separate the activated nickel from the sodium aluminate which appeared as a white suspension in the supernatant. The supernatant was then decanted and the activated nickel was washed and centrifuged successively with two 15-ml portions of distilled water and with two 15-ml portions of 2-propanol. The activated nickel was stored under 2-propanol and lasted at least three days without loss of activity.

Determination of sulphur in rapeseed oil. About 20 g of oil was accurately weighed into the reduction flask. The 2-propanol was decanted from a charge of catalyst, 10 ml of 2-propanol/5% H_2O was added and the mixture was transferred to the reduction flask. The flask was connected to the condenser and the nitrogen line was attached. A 150-ml beaker containing 50 ml of 1.0 N NaOH was placed under the bubbler tube so that the end of the tube was immersed in the NaOH solution. The nitrogen gas flow was adjusted to about one bubble per second. The flask contents were refluxed for about 1.5 hr. After refluxing, 50 ml acetone and a stirring bar were added to the 150-ml beaker and 20 ml of 60% HCl was added to the dropping funnel of the reduction flask. The

stirring rate was adjusted so that bubbles coming through the bubbler were broken up and dispersed through the absorber solution. The nitrogen gas flow was turned off and the HCl solution was slowly added to the reduction flask. The rate of addition was adjusted so that bubbles coming through the bubbler tube continued to be broken up and dispersed.

Dithizone indicator solution (0.5 ml) was added to the 150-ml beaker and the solution was titrated with the mercuric acetate solution using the 2.000-ml micrometer burette. To minimize effects of oxidation, the titration was carried out gradually as the H_2S was being evolved. The titrant was added in 5-µl aliquots and the endpoint was reached when the colour changed from yellow to purple-red. When the nickel was completely digested, the flask contents were refluxed and the nitrogen was turned on to a flow rate of about 2 bubbles per second. The titration was continued until no further sulphide was evolved. The nitrogen flow was then turned off and the heating mantle was removed from the flask. At this point the flask was cooled causing the absorber solution to be drawn up into the bubbler tube. This removed any sulphide absorbed on the glass walls of the bubbler tube. The amount of absorbed sulphide was usually negligible but in cases where it was significant the entire apparatus was rinsed with the absorber solution before the titration was completed.

The sulphur concentration of the oil was calculated as follows:

$$\text{ppm Sulphur } ({}^{W}/_{W}) = \frac{(X-Y) \times F}{W}$$

X = mercuric acetate (µl) required to titrate sample.

Y = mercuric acetate (µl) required to titrate reagent blank (the above procedure omitting the sample).

F = factor (about 1.0); the amount of sulphur (µg) titrated per µl of mercuric acetate titrant. This factor was determined experimentally by analysis of pure sulphur compounds and corrects for the slightly low recovery (about 95%).

W = the weight of the sample in grams.

Determination of sulphur in commercial nickel catalysts

Approximately 0.2 g of catalyst was weighed into the reduction flask of the Raney nickel reduction apparatus. Twenty milliliters of 2-propanol/5% H_2O were added and the apparatus was assembled. The nitrogen flow was started and the determination was carried out as in the Raney nickel procedure described for rapeseed oil.

Laboratory extraction of rapeseed

The "Swedish extraction method" of Troeng (66) was used with minor modifications to obtain oil samples from rapeseed

in the laboratory. Approximately 5 g of seed were weighed into a 60-ml stainless steel tube. Three ball bearings (3/4 in. diameter) and 4 ml "Skelly F" petroleum ether were then added and the tube was stoppered with a fluorosilicone rubber stopper. The tube was shaken longitudinally in a shaking machine at 200 cycles per min (4 cm displacement) for at least 12 hr. After shaking, the extract was filtered through Whatman No. 2 V-fluted filter paper and the tube was rinsed with three 40-ml portions of solvent. The combined filtrate was collected in tared 150-ml beakers and evaporated to constant weight at 60° C. After weighing, samples were transferred to 10-ml sample vials for storage. The samples were representative of the total seed oil but only 85-90% of the oil was recovered due to insufficient washing of the meal.

Originally, neoprene rubber stoppers were used for the extraction tubes. It was found, however, that 400-600 micrograms of sulphur were extracted from the neoprene stoppers during the procedure. No contamination was found when fluorosilicone rubber stoppers were used.

V. RESULTS AND DISCUSSION

Determination of sulphur in rapeseed oil

Three possible methods were considered in this study. Two methods, flask combustion and tube conbustion, involve complete oxidation of the sample and conversion of sulphur to sulphate. The Raney nickel method involves desulphurization on a hydrogenation catalyst and formation and determination of hydrogen sulphide.

Flask combustion method. This method was relatively simple and rapid. Difficulties were encountered since the small sample size and low sulphur concentrations resulted in the formation of very small quantities of SO_2 and SO_3. Because of the dilution effect of the absorbing solution, most samples were below the detection limits of the turbidimetric method. Although the colourimetric method had a lower detection limit, it was very sensitive to cationic impurities as well as to pH and phosphate. It was necessary to remove interfering ions by ion exchange procedures and to adjust the pH with buffer. It was also very difficult to find a support on which the oil would be oxidized. Paper, cotton, and gelatine capsules contained too much sulphur. Glass wool melted and ruined the combustion head, while quartz wool was too

brittle. Small quantities of sulphur oxides were absorbed on the flask surface. The method was abandoned after preliminary testing indicated that the limit of detection was about 100 ppm.

Tube combustion method. Pippen and Mecchi (52) used a tube combustion procedure and found recoveries ranging from 70% to 90% for samples containing 5-20 µg of sulphur.

Attempts to combust rapeseed oil in combustion tubes of similar design were unsuccessful even when pure oxygen at 950° C was used. Quantities of oil remained uncombusted and were converted to black tars and crystalline waxy material which appeared to contain large quantities of polyaromatic hydrocarbons. The reduction procedure for determination of sulphate, although sensitive and specific, was laborious and time consuming - especially the evaporating steps. Also variable amounts of sulphur oxides were absorbed on the catalyst and glass walls of the apparatus and were released at undetermined times, thus leading to non-systematic errors in analysis.

Raney nickel reduction method. Baltes (9) described a method for the determination of 0.5-100 ppm sulphur in commercial marine oils using the Raney nickel reduction procedure of Granatelli (25). Baltes suggested that nickel catalysts could be utilized for the desulphurization of rapeseed

oil prior to hydrogenation. Babuchowski and Zadernowski (8) demonstrated that 0.9-100 µg sulphur could be determined in rapeseed oil using the same method. They tested KCNS, cysteine, methionine, and 5-vinyl-2-thiooxazolidone and found recoveries ranging from 97-99% at the 100-µg level.

Briefly, the method involves desulphurization of the sulphur compounds over a Raney nickel catalyst. The sulphur is irreversibly adsorbed onto the active sites of the Raney nickel surface and released as H_2S on digestion of the nickel in strong acid. The H_2S is collected in a caustic acetone solution and titrated with mercuric acetate using dithizone as an indicator. About 2.5 hr is required for a single determination.

Several alterations were made from the method of Granetelli (25). The first was in the preparation of the Raney nickel catalyst. It was found more convenient to prepare the catalyst charges in advance rather than in situ. Catalyst prepared in situ is very difficult to free from all traces of sodium aluminate. This compound tends to precipitate on the flask during addition of acid, probably as alumina, and the construction of the flask makes it very difficult to remove this precipitate. This difficulty was best avoided by preparing the catalyst outside the reduction flask as described, the catalyst thus prepared being essentially free from sodium

aluminate. This method also saved time since several charges of catalyst could be prepared in advance.

The second alteration was the addition of a reflux condenser between the reduction flask and the absorbing solution. This not only prevented extraneous material from being carried over into the absorbing solution, but also prevented the loss of volatile sulphur components, such as isothiocyanates, from the reduction flask. The loss of sulphur was found to be quite extensive if the condenser was not used.

The third alteration was in the design of the absorber. Baltes (10) and Babuchowski (8) favoured the absorber described by Granatelli (25). This type of absorber is perhaps useful when small flow rates of carrier gas are used. Fensom et al (23) recommended the use of fritted glass bubblers but it was found difficult to draw the solution back through these to dissolve any sulphide trapped in the bubbler tube. The use of a bubbler equipped with many small holes in combination with rapid stirring of the absorbing solution was found to give the best results.

Calibration of the Raney nickel method. For all sulphur calibration work, the Raney nickel method was followed with changes as below.

Since Granatelli (25) reports an incomplete recovery of sulphur, analysis of known quantities of a standard aqueous KCNS solution was carried out as follows. Aqueous portions of a 350-ppm sulphur solution (KCNS) containing 35-700 µg of

sulphur were added to 20-ml portions of 2-propanol/5% H_2O. The sulphur contents of these solutions were determined by the Raney nickel method (Table 6). The mean recovery was found to be 94% (SD = ± 5%).

In order to determine the effect of rapeseed oil on the recovery, samples of deodorized oil weighing 15-25 g were analyzed for sulphur. Before reduction, aqueous portions of the KCNS solution were added as above to the mixture. The figures for sulphur found (Table 7) were corrected for the 0.6 ppm S originally present in the oil. Recovery was not affected by the presence of the oil.

Since the recovery of sulphur was consistently less than 100%, a correction factor (0.94) was used in all further calculations. This factor is in agreement with the factor 0.95 reported by Granatelli (25).

In order to assess the suitability of the method for various types of sulphur compounds, small quantities of different sulphur compounds were determined in the presence of 15-25 g of rapeseed oil in the manner described above for KCNS. Where possible, the standard was made by dissolving the compound in the oil; in most cases, however, it was necessary to use an alternative solvent, usually water, to prepare the standard. Recoveries of over 90% were obtained for all compounds tested except methyl methane sulphonate which

TABLE 6

Recovery of sulphur from KCNS

Sulphur added (µg)	Sulphur found (µg)	Recovery (%)
0	0	
0	0	
35	32	91
35	29	83
69	68	99
69	65	94
140	125	89
140	130	93
350	340	97
350	340	97
690	660	96
690	680	99
	Average	94 (SD ± 5)

TABLE 7

Effect of rapeseed oil on recovery of sulphur from KCNS

Oil added (g)	Sulphur added (micrograms)	Sulphur found[a] (micrograms)	Recovery (%)
20.3	35	30	86
21.6	69	67	97
19.8	140	126	90
24.3	350	340	97
15.2	690	685	99
		Average	94 (SD ± 5)

a.Corrected for 0.6 ppm sulphur in added oil.

TABLE 8

Recovery of sulphur from various sulphur compounds

Compound	ppm S added	ppm S found[a]	Recovery (%)
Butyl isothiocyanate	4.6	4.4	96
	2.9	3.0	106
	2.4	2.6	109
	7.5	7.2	97
	9.6	8.7	90
	13.2	12.7	97
	13.6	13.5	99
4, 6-Diphenyl-pyran-2-thione	7.2	6.7	93
	4.1	3.9	96
Cysteine	13.0	12.5	96
	16.4	16.2	99
Dimethyl-sulphoxide	17.6	16.6	94
	49.0	45.6	93
Methyl methane sulphonate	17.5	2.1	12
	18.8	0.4	2

[a] Corrected for 0.6 ppm S originally present in the oil. Calculated with recovery factor 0.94.

TABLE 9

Effect of crude oil impurities on recovery of sulphur

Sulphur added µg	Sulphur found[a] µg	Sulphur from crude oil µg	Adjusted recovery[b] (%)
388	720	350	95.0
223	402	186	97.0

a. Calculated with recovery factor 0.94.

b. $\text{Adjusted recovery} = \frac{(\text{Sulphur found} - \text{sulphur from crude oil})}{\text{sulpher added}} \times 100$.

did not react appreciably (Table 8).

Even using the established recovery factor 0.94, recoveries of less than 100% were obtained in the above experiment. The low recoveries are most likely due to the sulphur compounds analysed being less than 100% pure.

In order to assess the effect of crude oil impurities on the method, samples of crude oil, previously analysed by the Raney nickel method, were mixed with known amounts of sulphur (butyl isothiocyanate). Recovery of the added sulphur was 96% (Table 9). It is reasonable to assume, therefore, that impurities normally occurring in the oil have little or no effect on the recovery of sulphur.

Effect of processing on the sulphur content of the oil

The processing of rapeseed oil to produce salad or cooking oil involves the sequence of steps shown in Table 10. Oil samples from different processing steps were obtained from two different processors, both of whom used the prepress-solvent method of extraction. For reasons of confidentiality the processors are designated A and B. These samples represented Oro, Echo, and Span varieties. The sulphur content of each sample was determined by the Raney nickel method (Table 10). The results compare favourably with previous results reported by von Fellenberg (Table 3).

Expelled and extracted oils. Expelled oils contained 19-25 ppm sulphur. They appeared to have fairly uniform colour and very little gum.

TABLE 10

Sulphur content (ppm) of commercially processed oils[a]

Oil sample	Oro Fall 71[c] Plant A	Echo Fall 71 Plant B	Span Fall 71 Plant B	Span Spring 72 Plant B	Span Spring 72 Plant A
Expelled	19	21	25		
Extracted	57	10	33		
Crude	31	18[b]	27[b]	17	17
Degummed	16				
Refined	7	4	9		
Bleached	5	3	4		
Deodorized	1	1	1	1	1

a. Means of two or more analyses.

b. Calculated from results for expelled and extracted oils.

c. The words spring and fall denote the time of crushing.

The sulphur content of the extracted oils was more variable, however, and appeared to depend on the colour of the oil and on the amount of gum present. Extracted Oro oil (from plant A) contained the largest amount of sulphur, 57 ppm, and also the most gum. The gum from this sample separated from the oil on standing and was further concentrated by centrifugation. The centrifuged gum fraction amounted to 6% of the total oil by weight and contained about 385 ppm sulphur. The oil fraction, after removal of the gum, contained only 33 ppm sulphur. These results are in agreement with those of André (3) and von Fellenburg (22), who noted that the sulphur content of rapeseed oil seemed to be concentrated in the nonsaponifiable portion.

The solvent-extracted Span oil from plant B contained little gum but was dark brown in colour. This sample contained 33 ppm sulphur, the same as the above Oro sample after removal of the gum. The solvent-extracted Echo oil from plant B was light yellow in colour and contained no gum. This oil contained only 10 ppm sulphur.

The above results indicate that a large portion of the sulphur in rapeseed oil is extracted into the oil along with the more polar gum constituents. Norris (50) noted that the phosphatide and nonsaponifiable portions of oils appear mostly during the last stage of the extraction process. Refining losses from oil collected at this stage may be as high as 80%.

Careful attention to the most suitable degree of extraction may therefore provide an oil of superior quality with lower gum and sulphur content.

Crude oil. Crude oil is the combined expelled and solvent extracted oils. Since crude oils for the Echo and Span seed samples (Fall 71) processed by plant B were not available, the sulphur contents of the crude oil for these samples were calculated from the sulphur contents of the expelled and solvent extracted oils, assuming that the crude oil consisted of 70% expelled oil (personal communication, from one of the processors). The sulphur contents of the crude oils again appeared to be related to the colour and gum content of the oils. Samples containing more colour and gum, Oro (Plant A, fall 71) and Span (Plant B, fall 71), also contained more sulphur.

Degummed and refined oil. Only one sample (Oro, plant A) was degummed, presumably because of the high gum content of the crude oil. Degumming lowered the sulphur content of this oil from 31 ppm to 16 ppm. This degummed oil was comparable in colour, gum content, and sulphur content to the crude Span oils from plants A and B (Spring 72) which originally had less colour, gum, and sulphur content.

Caustic refining further lowered the sulphur content of the oils to 4-10 ppm, the final value apparently depending

on the original sulphur content of the crude or degummed oil. The removal of sulphur by degumming and refining probably depends on the formation of oil-insoluble miscella in which the sulphur compounds are concentrated. Some oil-insoluble compounds of the $Na^+ RS^-$ type may also be formed during caustic refining.

Bleached oil. Conventional bleaching with activated earths lowered the sulphur content of the refined oils to 3-5 ppm. This probably occurs through the adsorption of electronegative sulphur on electropositive sites on the bleaching clay. Bleaching with deactivated nickel catalysts has been reported to completely remove sulphur from oils, as well as to reduce the oil colour as efficiently as with conventional bleaching clays (50).

Deodorized oil. Deodorization lowered the sulphur content of the oils to about 1 ppm. Presumably, deodorization is effective only for sulphur compounds with relatively low boiling points such as the isothiocyanates.

Effect of hydrogenation on the sulphur content of the oil

Oils for the production of fats such as margarine and shortening are processed in the same manner as for salad or cooking oils except that, after refining, the oil is hydrogenated. Although the hydrogenation process also bleaches the oil, some oils are bleached before hydrogenation.

The sulphur content of samples of refined oil, hydrogenated oil, and fresh and used catalysts was determined. Almost all the sulphur in the refined oil was removed in the hydrogenation process (Table 11). The loss in sulphur from the oil was approximately equal to the increase in sulphur content of the catalyst. The rather large sulphur content of the used catalyst (0.6%) would be sufficient to cause significant reduction in hydrogenation rate if the catalyst was used a second time. A large increase in specificity as well as in the extent of cis-trans isomerization (31) would also be expected if the sulphur-containing catalyst were used again.

The refined oils in this study contained 4-9 ppm sulphur (Table 10). Even with this amount of sulphur more processors would have to use more catalyst for hydrogenation than they would normally use for a comparable sulphur-free oil under similar conditions. Also, the catalyst could not be used more than once or, at most, twice. Even using extra catalyst, large changes in hydrogenation rate, specificity, and relative rate of cis-trans isomerization would probably take place as the hydrogenation proceeds. Since the sulphur content of the refined oils is not mornally known to processors, the amount of catalyst used has to be arbitrarily estimated. If the sulphur content should be too high, the oil might not be hydrogenated properly and the process would have to be repeated. Removal of sulphur from the oil before hydrogenation, either by deodorization or by contact with used catalyst, may aid processors in developing a more uniform and economical hydrogenation process.

TABLE 11

Effect of industrial hydrogenation on the sulphur content of rapeseed oil and catalyst

Oil	Sulphur content of oil (ppm)	Catalyst	Sulphur content of catalyst (ppm)[a]
Unhydrogenated	8	Fresh	520
Hydrogenated	1	Used	6400

a. As ppm sulphur in nickel.

Effect of seed condition on the extraction of sulphur into the oil

Some of the conditions which could influence the extraction of sulphur with the oil were studied with samples of high-glucosinolate (Oro) and low-glucosinolate seed-types (courtesy Dr. B. R. Stefansson). The oils were extracted in the laboratory by the Swedish extraction procedure.

Effect of heating of the seed. Rapeseed is usually heated prior to industrial oil extraction partly in order to inactivate the enzymes which cleave glucosinolates when the seed has been crushed. To observe the effect of heating on the sulphur content of the oil, oil was extracted from samples of high-glucosinolate (Oro) seed which had been heated at 120° C for 12 hours. Oil was also obtained from a sample of unheated seed. Surprisingly, the oil from the unheated seed contained no sulphur while the oil from the heated seed contained 16 ppm sulphur (Table 12). To verify these results, a further sample of Oro seed was heated, this time for 144 hr at 120° C. The oil extracted from this sample contained 84 ppm sulphur. A sample of low-glucosinolate seed also was heated at 120° C for 12 hr before extraction. No sulphur was detected in the oil extracted from this seed.

The above results are not what was originally expected. Since no sulphur was detected in the oil from the heated low-glucosinolate seeds, the sulphur in the oil from the heated high-glucosinolate seeds most likely originates from the glucosinolates. Also the sulphur in the oil of the heat-treated seeds is probably in the form of oil-soluble compounds produced on thermal degradation of glucosinolates. Both glucose and sulphur are known to be chemically reactive at 100° C. Since commercial processors only heat rapeseed for a short period of time at much lower temperatures, this effect is probably not important to their operation.

The absence of sulphur in the oil from unheated high-glucosinolate seed is difficult to explain since enzyme action would presumably release isothiocyanates as the seeds were crushed. To allow some time for enzymatic action to take place with no influence from solvent, samples of high-glucosinolate seed were crushed for various periods of time before extraction. Even with 30 minutes of crushing before extraction, only a trace of sulphur was found in the oil. (Table 13). Possibly, the isothiocyanates are not sufficiently soluble in the oil to be extracted from the meal. This situation may be promising for industrial application.

Effect of moisture. Seeds with high moisture content have been reported to yield oils with increased amounts of polar material (60); consequently, a higher sulphur content would be expected in these oils. Known amounts of water were added

to 5-gram portions of seed before extraction by the Swedish Method. Addition of more than 5% moisture to unheated high-glucosinolate seeds resulted in the extraction of large quantities of sulphur with the oil. This effect was not observed to the same extent with heated seeds or with low-glucosinolate seeds (Table 14). The sulphur content of the oil from heated seeds with added water was higher than with no added water. The increase in sulphur content in the oil from seeds with added moisture could be due to a combination of increased enzyme activation and the extraction of increased amounts of polar materials into the oil. The results from this study indicate that the moisture content of the seed may be a critical factor in determining the amount of sulphur that will be extracted into the oil.

Effect of damaged or green seeds. Oil was extracted from samples of green seed and seed which had been damaged by heat or frost. In each case relatively large amounts of sulphur were found in the oil (Table 13). These results indicate that the seed quality is also important in determining the amount of sulphur extracted into the oil.

Effect of glucosinolate content. As previously described, seeds with low glucosinolate content were subjected to various conditions of heating and moisture. The oil from heated seed contained no detectable sulphur while the oil from moistened seed contained only about 10 ppm sulphur (Table

TABLE 12

Effect of seed heating on the sulphur content of the oil

Glucosinolate content of seed	Heating time (hr at 120°C)	Sulphur in oil (ppm)
High[a]	0	none detected
"	12	16
"	144	84
Low[b]	12	none detected

a. Oro.

b. Courtesy Dr. B. R. Stefansson.

TABLE 13

Effect of damaged or green seeds on the sulphur content of the oil

Glucosinolate content of seed	Type of damage	Sulphur in oil (ppm)
High[a]	Crushed for 5 min[c]	trace
"	" " 15 "	"
"	" " 30 "	"
High[b]	75% green[d]	50
"	40% frost[d]	18
"	Heated[d]	8

a. Oro.

b. Unknown variety.

c. Crushed in tubes immediately before extraction.

d. Commercial seed described as green, frost, or heated quality by the Grain Research Laboratory.

TABLE 14

Effect of seed moisture content on the sulphur content of the oil

Glucosinolate content of seed	Heating time (hr at 120°C)	Moisture added[c] (%)	Sulphur in oil (ppm)
High[a]	0	0	none detected
"	0	2	8
"	0	4	16
"	0	6	58
"	0	10	88
"	0	19	467
"	12	5	50
"	12	10	37
"	12	14	41
Low[b]	0	4	12
"	0	5	10
"	0	8	11

a. Oro.

b. Courtesy Dr. B. R. Stefansson.

c. As percent by weight in addition to the original moisture contents which were 5% (high glucosinolate seed) and 4% (low glucosinolate seed).

12 and 14). These results indicate that development of an acceptable low-glucosinolate seed type may lead to fewer sulphur problems for processors.

VI. CONCLUSIONS

Method for determination of sulphur

A method for the determination of sulphur in rapeseed oil based on the Raney nickel reduction method described by Baltes (9) and Babuchowski and Zadernowski (8) has been adapted. The nickel sulphide formed by reduction of sulphur compounds with Raney nickel is digested in strong acid. Hydrogen sulphide is released and is trapped in dilute caustic solution where sulphide ion is titrated with Hg^{+2} ion using dithizone as an indicator.

For a 20-g sample of oil, the useful range is 1-50 ppm. with a detection limit of about 0.5 ppm. The precision (±2 SD) is about ±10% above the 10 ppm level and about ±1 ppm below the 10 ppm level. A complete analysis, excluding preparation of catalyst, takes about 2 hr. Compounds containing sulphur in oxidation states higher than two may not be reduced although this may not be important since it seems unlikely that these compounds will be present in rapeseed oil.

Since the method is relatively simple and precise and its useful range is suitable for work with rapeseed oil, the method may be useful in industrial laboratories. Although a

fairly long time is required to complete a single analysis, it is feasible to perform several analyses simultaneously as long as the requisite bench space and equipment are available. The apparatus is relatively cheap.

It may be desirable to improve the precision of the method for samples containing 1-10 ppm sulphur since this range seems to be critical to processors. It is not feasible to increase the sample size beyond about 25 g and thus it is necessary to either find a more sensitive method for sulphide detection or improve the endpoint detection. Endpoint detection could be improved by using a photometric titration, while sensitivity could be improved by adapting the methylene blue method of Pippen and Mecchi (52). The methylene blue method has the advantage of being specific for sulphide. Both methods, however, require the use of more complex equipment and their usefulness may be limited by the efficiency with which H_2S is trapped in the absorbing solution.

Effect of industrial extraction and processing on the sulphur content of the oil

Although the amounts of sulphur found in expelled oils was fairly constant, the sulphur content of solvent extracted oils was variable and seemed to depend on the amount of gums and dark coloured materials present in the oils. Oils that were light coloured and contained no visible gums contained the

least amounts of sulphur. The wide variation in colour, gum and sulphur content of the oils examined suggests a need for more study on industrial extraction procedures, especially on the effect of extraction efficiency on the quality of the oil extracted.

The amount of sulphur found in different degummed, refined, and bleached oils was approximately proportional to the sulphur content of the crude oils. Deodorization lowered the sulphur content to about 1 ppm. It may be useful to determine the sulphur content of the crude oil before refining and to investigate methods to increase the efficiency of removal of sulphur from oils, especially from crude oils with high sulphur contents.

Hydrogenation lowered the sulphur content of refined oils to about 1 ppm. Most of the sulphur was found on the nickel catalyst after hydrogenation. Since the presence of large amounts of sulphur on the catalyst may lead to difficulties in hydrogenating, it may be useful to monitor the sulphur content of oils before hydrogenation. It may be more useful, however, to investigate methods such as treatment with used catalyst or deodorization which could result in complete removal of sulphur from the oil before hydrogenation.

Effect of seed conditions on the extraction of sulphur into the oil

Even if the seeds were damaged by crushing before the extraction, laboratory extraction of unheated seeds gave sulphur-free oil. Moisture, frost damage, greenness, or excessive heating resulted in increased

amounts of sulphur in the oil. Extraction of low-glucosinolate types of rapeseed resulted in lower amounts of sulphur in the oil than from high-glucosinolate types. These results indicate that it may be possible to produce even crude oils of low sulphur content provided proper attention is given to seed quality and seed treatment. The expected introduction of low-glucosinolate seed types should result in a further lowering of the sulphur content of the oils.

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