

SULFUR LEVELS IN CANOLA OILS FROM CANADIAN CRUSHING PLANTS: ANALYSIS BY RANEY NICKEL REDUCTION AND INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROSCOPY

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INTRODUCTION

Canola and rapeseed oils are well known for containing small amounts of sulfur compounds (Gobel and Franzke 1975; Daun and Hougen 1976; Krygier and Gawinowski 1983; Abraham and deMan 1987). These components are considered to derive from glucosinolates (Franzke et al. 1975; Daun and Hougen 1977; Devinat et al. 1980;). Some sulfur compounds have been associated with poisoning of catalyst used in hydrogenation of canola oil (Drozdowski et al. 1973; Hougen and Daun 1983; deMan et al. 1983). Utilization of cultivars with low levels of glucosinolates (canola) has resulted in a decrease in the sulfur levels in crude oils (Hougen and Daun 1983) but the problem was still sufficiently severe for the Canadian industry to introduce a maximum level of 10 mg/kg sulfur in crude oils. This has recently been lowered to 8 mg/kg (Canadian General Standards Board 1987). Although it is known to determine only a part of the total sulfur in rapeseed oils, a method involving reduction of sulfur with Raney nickel is specified in the Canadian Standard as it has been recognized that results from this method relate closely to problems caused by catalyst poisoning (Hougen and Daun 1983; Abraham and deMan 1987).

Inductively coupled plasma atomic emission spectroscopy (I.C.P.A.E.S. or I.C.P.) has presented a new potential method for determination of sulfur in rapeseed and canola oils. This paper gives results for samples of canola oil produced in Canada analyzed by both reductive (Raney nickel) and I.C.P. methods. Data on the Raney nickel sulfur content of canola oils from Canadian crushing plants over the period 1979 to 1989 are also presented.

MATERIALS AND METHODS

Industrially extracted oils at different stages of processing were obtained from an oilseed crushing plant in Ontario (Plant A) and Alberta (Plant B) over the period of June to September, 1990. Both plants provided pressed, solvent extracted, and degummed canola oils. All oils were analyzed for sulfur content by Raney nickel and inductively coupled plasma atomic emission spectrometer (I.C.P.) methods. In the longer term study, samples of crude, degummed, and occasionally solvent extracted and pressed oils were received from Canadian crushing plants on a random basis over the period 1979 to 1989. Random samples were selected on an equal plant basis for determination of reducible sulfur.

In the reducible sulfur method (Daun and Hougen 1976) 15-20 g of canola oil was refluxed with 1 g of activated nickel-aluminum (Raney nickel) to reduce divalent and some tetravalent organo-sulfur compounds to nickel sulfide. Addition of hydrochloric acid released hydrogen

sulfide which was trapped in a sodium hydroxide solution and titrated with mercuric acetate using dithizone as indicator. The use of a reflux condenser inserted between the reduction flask and the gas trapping solution reduced the loss of volatile sulfur compounds during the reduction. A set of sulfur standards (3, 6, 9, 12, and 15 mg/kg) was prepared by dissolving a known amount of dibenzylidissulfide in a known weight of deodorized canola oil. These standards were used to determine a sulfur recovery factor for the apparatus used. After correction for the small amount of sulfur in the blank oil, recovery of sulfur from dibenzylidissulfide was generally greater than 90%.

For I.C.P. analyses, 5 g of oil was weighed into a 10 ml volumetric flask and diluted to volume with xylenes (BDH Analar). A Gilson Minipulse 2 pump with a Maximum Dissolved Solids Nebulizer (MDSN) was used to introduce the samples to an ARL 3410 I.C.P. with minitorch and a nitrogen purged monochrometer. The emission spectra were measured with a holographic 2400 groove/mm grating. A stock solution of sulfur in oil was prepared by dissolving a known weight of dibenzylidissulfide in a known weight of warm blank oil (noname baby oil, Sun Fresh Limited). Standards were then made by weighing stock solution into a 50 ml vol flask, adding blank oil until a weight of 25 g was reached, and then filling to volume with xylenes. Sulfur was measured by its emission at 180.731 NM.

Instrument parameters were:

Incident Watts	700
Photo Multiplier Tube Attenuation	11
Integration Time (Sec.)	1.0
Argon Flows (l/min)	
Coolant	12
Plasma	0.8
Carrier	0.6
Sample Transport	
Pump (digits)	700
Flow Rate (ml/min)	2.4

The detection limit was 0.5 mg/kg sulfur.

RESULTS

Comparison of Raney Nickel Sulfur and Total Sulfur by I.C.P.

In general, the I.C.P. method gave higher results than the reducible sulfur method. For all samples in the study, there was a linear relationship between the two methods with the I.C.P. method giving about 1.6 times more sulfur than the Raney nickel method (Fig. 1). The difference between the two methods was most pronounced with solvent extracted oils. The I.C.P. method required considerably less time (38 samples in 2 days) than the Raney nickel method (38 duplicate analyses in 4 weeks assuming 2 sets of apparatus). Mean differences between Raney nickel and I.C.P. results were as follows:

Oil Type	I.C.P. Sulfur mg/kg			Raney Nickel Sulfur mg/kg			Paired Diff.		
	Mean	Min.	Max.	Mean	Min.	Max.	Mean	T	Pr> T
Solvent	28.8	16.2	67.3	19.7	14.5	33.6	9.1	4.88	0.0006
Pressed	13.9	11.0	16.2	11.0	8.7	16.4	2.8	3.70	0.0041
Degummed	7.8	3.9	12.7	6.9	4.6	10.0	0.9	3.07	0.0077

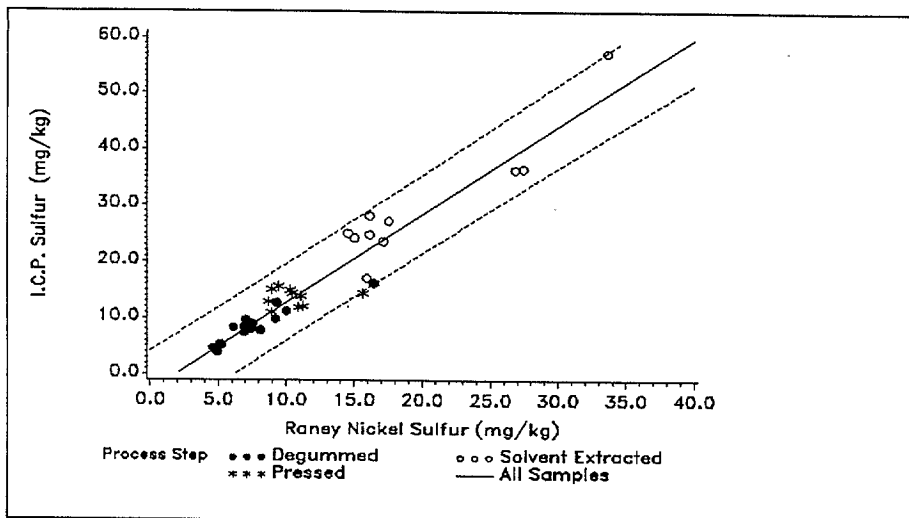


Figure 1. Relationship between sulfur determined by I.C.P. and Raney nickel sulfur for samples from two Canadian crushing plants. Regression coefficients: all samples $r^2=0.9064$, slope= 1.57; degummed oils $r^2=0.8222$, slope=1.35; extracted oils $r^2=0.8102$, slope=1.62; pressed oils $r^2=0.0544$, slope=0.25.

Sulfur varied between crushing plants. Analysis of variance using the general linear model because of the unbalanced design showed the difference was only in the level of sulfur in the solvent extracted oils.

Oil Type	Plant	I.C.P. mg/kg LS Mean	Plant Diff. Pr > T	Raney mg/kg LS Mean	Plant. Diff. Pr > T
Degummed	A	8.5		7.1	
Degummed	B	7.2	0.5242	6.6	0.6316
Pressed	A	14.7		11.3	
Pressed	B	11.7	0.2793	10.3	0.4833
Solvent	A	23.3		16.1	
Solvent	B	43.4	0.0001	29.3	0.0001

Changes in Raney Nickel Sulfur Levels Since 1979/80.

Analysis of samples collected from Canadian Crushing Plants over the period 1979 to 1990 showed that, while the level of sulfur in solvent extracted and crude (combinations of pressed and solvent extracted oils) oils had not changed, the level in degummed oils had dropped significantly. The lower level of sulfur in crude oils for the years 1982 to 1985 is a result of only one or two plants participating in the study at that time and serves to emphasize the large between plant variation. Examination of the data for degummed oils showed that the range in results had also been reduced significantly (Fig. 2).

Year	No. of Samples	Mean Sulfur Degummed mg/kg	No. of Samples	Mean Sulfur Crude mg/kg	No. of Samples	Mean Sulfur Solvent mg/kg
1979	22	15.7	8	15.3	14	12.3
1980	35	14.6	11	11.1	16	19.1
1981	2 ^a	18.5	3 ^a	14.3		
1982			3 ^a	5.9		
1983			1 ^a	7.1		
1984	1 ^a	4.0	1 ^a	4.9		
1985	4 ^a	6.0	2 ^a	5.8		
1986	5 ^a	6.0	5 ^a	9.8		
1987	11	5.5	7	10.8		
1988	8	7.2	4	10.7		
1989	7	7.2	8	19.9		
1990	16	6.9	11	17.5	11	19.7

^a Yearly composites by plant.

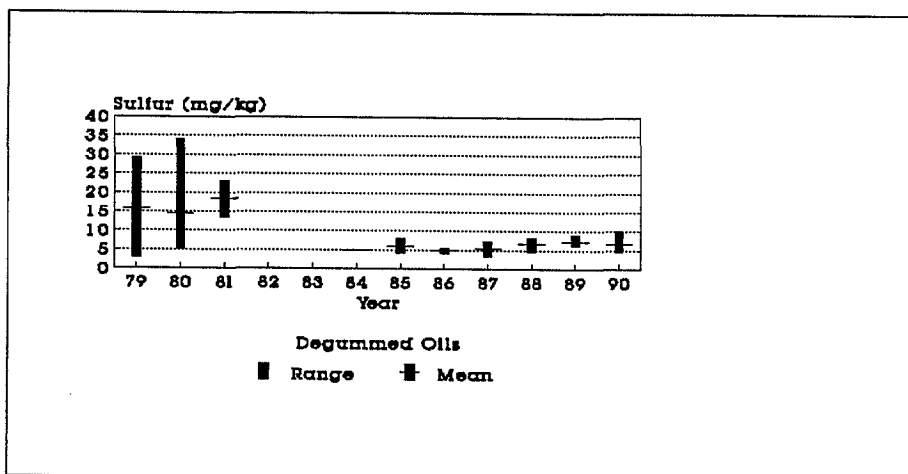


Figure 2. Range in Raney nickel sulfur levels for degummed oil samples produced by Canadian Crushing Plants, 1979-1990.

DISCUSSION

Comparison of Raney Nickel Sulfur and Total Sulfur by I.C.P.

There have been two main ways of determining sulfur contents of canola and rapeseed oils. The Raney nickel method involves reduction of sulfur compounds with Raney nickel and analysis of hydrogen sulfide released during acidic digestion of the nickel. This method only determines that portion of the sulfur components which can be reduced under the analytical conditions, divalent, and to a certain extent, tetravalent sulfur (Daun 1973). Results from Raney nickel methods give results which are useful in predicting problems with hydrogenation (Hougen and Daun 1983; Abraham and deMan 1987). Similar sample types have yielded wide ranges in results for the Raney nickel methods as reported in different publications. For example, results for crude oils reported by Abraham and deMan (1987) are considerably lower than results from the Canadian Grain Commission for the same type of sample (Hougen

and Daun 1983, this work).

Methods that determine total sulfur (Halvarson and Hoffmann 1980, Abraham and deMan 1987) usually involve oxidation of the sample and determination of sulfur oxides produced. Results from these methods are higher than results from the Raney nickel methods and are less useful in predicting hydrogenation problems as they include sulfur components which are not implicated as catalyst poisons.

It would be expected that the I.C.P. method would give an estimation of the total sulfur content of the sample as it is theoretically capable of determining sulfur at any oxidation state. For samples analyzed in this project, the instrument was calibrated with dibenzylidissulfide, the same compound used to calibrate the Raney nickel method. Although the I.C.P. sulfur was consistently greater than the Raney nickel sulfur, the difference, especially in degummed oils, was not as great as the difference between total sulfur and Raney nickel sulfur reported by Abraham and deMan (1987). It is possible that the I.C.P. method does not account for all sulfur in the sample and recovery studies with this method should be carried out using compounds with sulfur at different oxidation states.

For degummed oils, the I.C.P. method gave sulfur levels only slightly higher than the Raney nickel method indicating that this method may be suitable for screening samples prior to hydrogenation. Further work is required using refined, bleached and deodorized oils.

Changes in Raney Nickel Sulfur Levels Since 1979/80.

Canola oil has been reported to contain less sulfur than rapeseed oil (Hougen and Daun, 1983) although the correlation between oil sulfur and seed glucosinolates was low. The present study includes samples collected from Canadian crushing plants over the period 1979 to 1990. This period includes the period 1979 to 1983 during which Canada completely converted from high-glucosinolate rapeseed to low-glucosinolate canola. The reduction in the average level of sulfur in degummed oils may be a reflection of the reduction of glucosinolates. The period 1982 to 1985 was also the time when Canadian crushing plants began to produce acid degummed oils. The effect on sulfur content of acid degumming versus water degumming is not known.

It is notable that the main difference between processors was in the solvent extracted oils (and hence crude oils). It would be interesting to determine whether this difference is due to the presence of sulfur in the extraction solvent (especially recycled extraction solvent) or to differences in processing conditions. Krygier and Gawinowski (1983) reported that recovered solvent contained considerably more sulfur than fresh solvent. In any case, the sulfur components causing the difference were removed during degumming of the oil in the degumming method used in Canada.

CONCLUSIONS

I.C.P. atomic emission spectroscopy was found to give higher results than the Raney nickel reduction method for sulfur contents of canola oils produced at Canadian crushing plants. The difference was most pronounced averaging 10 mg/kg for solvent extracted oils but averaged less than 1 mg/kg for degummed oils. This suggests that the I.C.P. method may be useful for screening oils prior to hydrogenation as it is a much more rapid method than Raney nickel reduction.

Sulfur levels (Raney nickel method) in degummed oils produced at Canadian crushing plants were found to have decreased from about 15 mg/kg in 1979/1981 to about 7 mg/kg since 1985. The range in sulfur levels has also been reduced. The reduction may be due to a combination of the introduction of low-glucosinolate canola varieties and possibly to the adoption of acid degumming.

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