Determination of Total Sulfur in Canola Oil

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A rapid and sensitive chromatographic method for the determination of total sulfur in canola oil is described. All forms of sulfur in the oil are quantitatively converted to sulfate in an oxygen bomb. The sulfate is separated from other ions and measured using an ion chromatograph equipped with a conductivity detector. Standards containing different forms of sulfur were prepared and analyzed with this method. Recovery achieved on 11 compounds covering the concentration range from 9.3 to 143.5 mg/kg S ranged from 95.7% to 102.2%. The coefficient of variability of total sulfur in canola oils ranged from 1.0% to 2.9%. Values obtained on high sulfur content mustard oils when plotted vs the values determined by barium precipitation method showed a correlation coefficient of 0.997 and provided a slope of 1.0. This new method employing comparatively simple equipment requires less than 40 minutes for a complete analysis and is reliable for the determination of as little as 0.5 mg/kg S in canola oil.

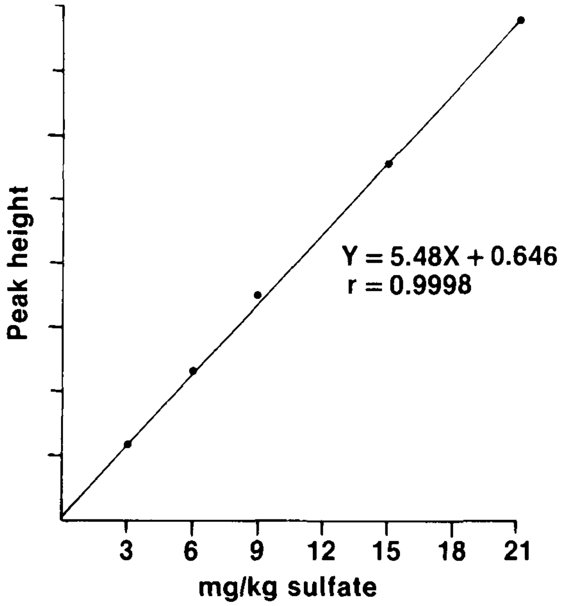

FIG. 1. Plot of the concentration (mg/kg) vs peak response for standard sulfate solutions.

Sulfur compounds have been implicated as hydrogenation catalyst poisons. Therefore, it is necessary to determine the amount of sulfur in canola oil which is widely used for hydrogenation purposes in Canada. Devinat et al. (1) divided the sulfur compounds in rapeseed into volatile, thermolabile and nonvolatile compounds. Several authors (2–4) reported different methods of identifying and determining volatile compounds in oils from the cruciferae family. Although the chemical nature of sulfur compounds in canola oil is not fully established, they are believed to be the hydrolysis products of glucosinolates present in the canola seed. During storage the glucosinolates undergo enzymatic decomposition producing isothiocyanates, thiocyanates and possibly sulfates and sulfides (5).

At present the canola industry relies on the use of the Raney nickel method (6) for the determination of sulfur in canola oil. This method is recognized as giving a good indication of the oil's capability for hydrogenation. It is known that the Raney nickel method measures only part of the sulfur present (7). In this method organically bound sulfur in nonolefinic hydrocarbon solutions is reduced to sulfide by specially prepared nickel catalyst. The addition of acid produces hydrogen sulfide which can be measured by titration with standard mercuric acetate using dithizone as indicator (8) or by colorimetry. Canola oil also contains other forms of sulfur compounds which are not adsorbed or chemically bound to Raney nickel.

TABLE 1

Analyses of Sulfur Compounds Using Ion Chromatography

Compound	Sulfur (%)	Recovery (%)	No. of determinations	Standard deviation
Allyl isothiocyanate	32.3	96.1	5	0.44
Butyl isothiocyanate	27.8	98.0	5	0.04
Cysteine	26.4	95.7	7	0.12
Heptyl isothiocyanate	20.3	95.7	5	0.54
P-methyl aminophenol sulfate	9.3	99.2	4	0.93
Phenethyl isothiocyanate	19.6	96.2	5	0.05
Sodium diethyl dithiocarbamate	28.4	97.1	6	1.54
Sodium dithionate	26.4	99.1	4	0.09
Sulfanilic acid	16.7	101.2	5	0.89
Sulfosalicilic acid	12.6	98.0	5	0.98
Toluene sulfonic acid	16.8	97.8	5	0.09

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Therefore, the above method is not suitable for determining total sulfur in oils.

The methyl thymol blue method has been used successfully in the past to determine sulfate in rain and waste water using an automated procedure (9,10). Cations other than barium form complexes with methyl thymol blue and interfere with the analysis. Potentiometric titration of sulfate using ion sensitive lead electrodes was proposed by Ross and Frant (11). Phosphate interferes with this analysis and has to be removed before sulfate can be analyzed. In the microcoulometric method sulfur dioxide is formed by combustion, and this reacts with the titrant ion which usually is kept constant (12,13). The decrease in titrant ion is amplified and recorded. The presence of halogens, nitrogen and sulfur trioxide interferes with the sulfur determination and may cause errors.

Combustion methods (14,15) followed by turbidimetry have been used successfully for the determination of sulfur in organic materials. The low sulfur content in canola oil makes it difficult to apply this method. During combustion, sulfur is quantitatively converted to sulfate. Hence, for total sulfur determination the first step is combustion. The problem is to measure the sulfate in the bomb extract with a high level of sensitivity.

Ion chromatography has emerged as a new technique for the determination of inorganic ions and was successfully applied for measuring chlorine in silicate rocks (16) and selected elements in oil shale (17). The use of ion exchange columns and a suitable eluent provides efficient separation and quantitation. The purpose of the present work was to determine the total sulfur in canola oil using the ion chromatographic technique after conversion to sulfate in an oxygen bomb.

MATERIALS AND METHODS

Canola oil samples were obtained from different industrial sources in Canada. Mustard oils were purchased from selected grocery stores. Ultra purity reagents were used wherever possible. Allyl, butyl, heptyl and phenethyl isothiocyanates and p-methyl aminophenol sulfate were bought from Eastman Kodak Co., Rochester, New York. Sulfosalicilic acid and cysteine were obtained from J. T. Baker Chemical Co., Phillisburg, New Jersey. Sulfanilic acid, sodium diethyl carbamate, sodium dithionate and toluene sulfonic acid were supplied by Fisher Scientific Co., Toronto, Ontario, Canada.

An oxygen bomb model 1108 (Parr Instrument Co., Moline, Illinois) was used for sample decomposition. The stainless steel bomb was equipped with a model 2901 ignition system. A sample of 1.5 g canola oil was placed in the stainless steel sample cup and 5 ml double distilled water was put in the bottom of the bomb. The nickel alloy fuse wire was connected to the loops as described by the manufacturer. After closing, the bomb was flushed several times with ultra pure oxygen. Finally the bomb was pressurized to 3030 kPa with ultra pure oxygen. After combustion, the contents were allowed to cool in running cold water for 15 min and the bomb slowly opened. The interior surfaces of the bomb and the combustion capsule were washed with a jet of double distilled water and degassed with a magnetic stirrer. The washings were made up to a predetermined volume, 50 ml for mustard oil and 15 ml for canola oil.

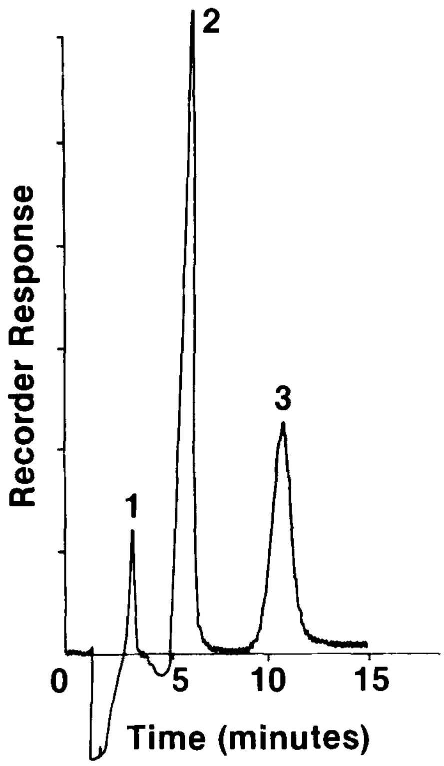

FIG. 2. Ion chromatogram of the bomb extract obtained by the combustion of crude canola oil. Identity of peaks: 1, chloride; 2, nitrate; 3, sulfate.

TABLE 2

Contents of Total Sulfur in Canola Oil Samples as Determined on Five Replicates by Ion Chromatography

Oil sample	Crude	Refined	Bleached and deodorized
Range mg/kg	23.6–24.1	19.1–20.2	15.6–16.5
Mean	23.8	19.7	16.2
Standard deviation	1.0	2.85	2.7

TABLE 3

Sulfur in Single Samples of Canola Oil as Determined by Ion Chromatography, Raney Nickel Method and Gas Chromatography

Sample	Ion chromatography method	Raney nickel method	Gas chromatography method
Crude	23.8	2.86	0.64
Refined	19.7	1.45	0.53
Bleached and deodorized	16.2	1.10	0.24

Each value represents the mean of 8 determinations for Raney nickel and gas chromatography method (volatile sulfur) and 5 determinations for ion chromatography. All values given in mg/kg.

TABLE 4

Comparison of Total Sulfur Determined by Ion Chromatography, Barium Precipitation and Raney Nickel Method for Five Mustard Oil Samples

Oil sample	IC method	BPT method	RN method
Indra	1.32	1.34	0.92
Royal mills	0.45	0.50	0.27
Lata	0.48	0.57	0.19
TRS	0.80	0.87	0.08
CTRS	0.19	0.20	0.01

Each value represents the mean of eight determinations. All values given in mg/kg.

A Waters Ion Chromatograph equipped with model 430 conductivity detector was used for the analysis. A strong anion exchange column IC-PAK TM was used in conjunction with a GUARD PAK pre column module and an LC pre column filter. The eluent was 1.48 mM sodium gluconate + 5.82 mM boric acid + 1.30 mM sodium borate + 12% acetonitrile + 0.25% glycerol. The flow rate was 1.2 ml/min^{-1}.

The washings from the bomb were first passed through a Waters SEP-PAK C18 cartridge to remove organics. The sample was then filtered through a millipore HA filter with 0.45 μm pore size to remove any particulates that may have been present. The filtered samples were injected into the ion chromatograph, and the peaks were compared with the calibration curve obtained using standard sulfate solutions. Sample sizes ranged from 25 to 200 μl, depending on the amount of sulfur present in the oil. Standard sulfate solutions were made by diluting a stock solution containing 60 mg/kg sulfate in double distilled water.

Raney nickel sulfur was determined by the method reported by Granatelli (8) with few modifications. Canola oil sample sizes ranged from 2 to 25 g, and 0.1% dithizone in acetone was used as indicator. The sulfur content by barium precipitation was measured by following the method of Bailey (15). The absorbance at 400 nm was compared with standard sulfate solutions made with double distilled water.

RESULTS AND DISCUSSION

Results obtained for the analysis of sulfur in a variety of sulfur compounds are shown in Table 1. These compounds included aliphatic and aromatic compounds, amino acids, sulfonated compounds, compounds with nitrogen and isothiocyanates. Sample sizes ranged from 0.07 to 0.11 g, and the sulfur content ranged from 9.3% to 32.3%. Average recovery ranged from 95.7% to 101.2%. In terms of mg/kg sulfur, the mean error obtained for samples containing 1 to 10 mg/kg was 0.1 to 0.4, for samples containing 10 to 100 was 0.3 to 3.9 and for samples containing 100 and above was 4.2 to 5.3.

Ion chromatography is essentially high performance liquid chromatography (HPLC) using specific stationary and mobile phases that are suitable for the separation of different ions. The conductivity detector used in this analysis measures the difference in conductivities of the eluting sample ions and the eluent ions. Smith et al. (18) reported a method of determination of sulfur and chlorine by ion chromatography using suppressor columns. The calibration curve was made by combustion of known amounts of s-benzyl thiuronium chloride. In this experiment standard solutions of sodium sulfate were used; the response is shown in Figure 1. The curve showing the concentration vs peak response had a correlation coefficient of 0.9998. Figure 2 shows an ion chromatogram of the bomb extract using crude canola oil. Three peaks were well separated, representing chloride, nitrate and sulfate. Carbonate is masked by the solvent peak and, as a result, it is not seen in the chromatogram. The sulfate peak is resolved quite well from the nitrate and chloride peaks. However, when the concentrations of chloride and nitrate were very large, the signal to noise ratio for sulfate was poor. Therefore, flushing of the bomb with ultra pure oxygen was carried out at least five times for the complete removal of air from the system. The sulfate ion had a retention time of 10.5 min, which was much higher than for chloride and nitrate. Reducing the buffer concentration increased the retention time and resulted in peak broadening, especially for sulfate.

The sulfur content of crude, refined and deodorized canola oils is given in Table 2. Five replicates were done of each sample, and the range, mean and standard deviation are presented. Addition of hydrogen peroxide in the bomb before combustion did not improve results. An oxygen pressure of 3030 kPa was sufficient to complete the oxidation. Neutralization of the bomb extract was not required because the system provided a wide and linear range with no pH limitations on eluent or sample for anion analysis.

The commonly used method for the determination of sulfur in canola oil is the Raney nickel method. Volatile sulfur compounds in oil are important because they are mainly responsible for the poisoning of the catalyst during vegetable oil hydrogenation. Table 3 shows a comparison of the Raney nickel sulfur, volatile sulfur and the total sulfur by the IC method for three canola oil samples. These results suggest that the Raney nickel sulfur represents only a small portion of the total sulfur present in the oil. According to Granatelli (8), this method measures only organically-bound sulfur in non-olefinic

TABLE 5

Sulfur Content of 12 Canola Oil Samples at Various Stages of Processing Using Three Methods

Sample number	Sulfur content (mg/kg)		
	IC method	RN method	GC method
1	11.8	2.0	0.436
2	13.3	1.1	0.531
3	8.8	0.2	0.000
4	17.5	1.3	0.291
5	15.1	1.2	0.285
6	15.7	1.2	0.322
7	15.5	1.0	0.170
8	10.3	0.9	0.155
9	9.6	0.9	0.118
10	9.0	0.8	0.088
11	8.2	0.6	0.020
12	6.6	0.2	0.10

TABLE 6

Sulfur Content of 13 Canola Oil Samples at Various Stages of Processing Using Three Methods

Sample number	Sulfur content (mg/kg)		
	IC method	RN method	GC method
1	16.5	0.36	0.128
2	9.5	0.29	0.118
3	6.8	0.23	0.111
4	4.5	0.02	tr
5	5.6	0.25	0.020
6	6.2	0.29	0.013
7	5.8	0.41	tr
8	13.6	0.20	tr
9	7.0	0.12	0.014
10	9.1	0.37	0.016
11	4.8	0.24	tr
12	5.6	0.00	0.000
13	5.5	0.00	0.000

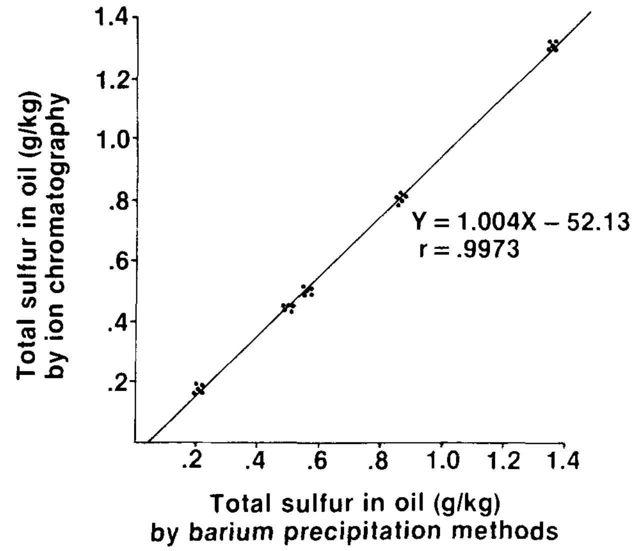

FIG. 3. Relationship of total sulfur content in mustard oil as determined by the barium precipitation and ion chromatography methods.

hydrocarbon solutions, and olefins in the sample may introduce an appreciable error. The decomposition products of glucosinolates include sulfates and sulfides which are not organically bound. The amount of volatile sulfur can be measured by the method reported by Abraham and deMan (4) using a gas liquid chromatograph equipped with a flame photometric detector.

The reliability of the present method was checked with the widely accepted barium precipitation method (15) for different mustard oil samples. Photonephelometric microdetermination of sulfate is suitable only for samples with relatively high sulfate concentration. Table 4 shows the amount of sulfur determined by the barium precipitation, Raney nickel and ion chromatography methods for mustard oils. The present method provided results identical to those obtained with the photonephelometric method, whereas the Raney nickel method gave much lower values. Tables 5 and 6 show the sulfur contents of two batches of oil at various stages of processing. The barium precipitation method is not suitable for canola oil because of its low sulfur content. Figure 3 is a plot of sulfur determined by the ion chromatography vs the photonephelometry method for five mustard oils. The correlation coefficient was 0.9973, and the slope of the regression line was 1.0. This indicates the method is applicable to oils containing a wide range of sulfur levels.

The Raney nickel method measures sulfur that poisons the Raney nickel catalyst. We suggest the use of the following terms for sulfur in canola oil: volatile sulfur, Raney nickel sulfur and total sulfur. The use of total sulfur should be restricted to that determined by a combustion method. The total sulfur method described is simple and sensitive. The microcoulometric method (12,13) using a Dohrmann microcoulometer is sensitive enough to use for canola oil. However, the equipment is expensive and highly specialized, and nitrogen compounds may interfere with the analysis. The method described in this paper can be used to determine total sulfur in canola oils with satisfactory precision and accuracy.

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REFERENCES

1. Devinat, G., S. Biasini and M. Naudet, *Rev. Fr. Corps Gras 27:*229 (1980).
2. Daun, J.K., and F.W. Hougen, *J. Am. Oil Chem. Soc. 54:*351 (1977).
3. George, P., and B. Torrgard, *Intern. Rapeseed Conf. Malmo, Vol. II:*348 (1978).
4. Abraham, V., and J.M. deMan, *J. Am. Oil Chem. Soc. 62:*1025 (1985).
5. Rutkowski, A., S. Gwiazda and K. Krygier, *Ibid. 59:*7 (1982).
6. Daun, J.K., and F.W. Hougen, *Ibid. 53:*169 (1976).
7. El-Shattory, Y., and J.M. deMan, *Can. Inst. Food Sci. Technol. J. 14:*53 (1981).
8. Granatelli, L., *Anal. Chem. 31:*434 (1959).
9. Lazrus, A.L., K.C. Hill and J.P. Lodge, in *Automation in Analytical Chemistry,* Medicad, Inc., 1966, p. 291.
10. Adamski, M., and S.P. Willard, *Anal. Chem. 47:*1191 (1975).
11. Ross, J.W., and M.S. Frant, *Ibid. 41:*967 (1969).
12. Killer, F.C.A., and K.E. Underhill, *Analyst. 95:*505 (1970).
13. Martin, R.L., and J.A. Grant, *Anal. Chem. 37:*644 (1965).
14. Toennies, G., and B. Bakey, *Ibid. 25:*160 (1953).
15. Bailey, J.J., and D.G. Gehring, *Ibid. 33:*1760 (1961).
16. Evans, K.L., and C.B. Moore, *Ibid. 52:*1908 (1980).
17. Nadkarni, R.A., and D.M. Pond, *Anal. Chim. Acta 146:*261 (1983).
18. Smith, F.A., A. McMurtrie and H. Galbraith, *Microchem. J. 22:*45 (1977).

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