

Leatherhead^{Food RA}

CONFIDENTIAL PROJECT REPORT

DVD 48

July 1995

THE DETERMINATION OF SULFUR IN
ANIMAL AND VEGETABLE OILS
I. LITERATURE SURVEY

Science and Technology Group

RESEARCH REPORT

1995-5

First Confidential Project Report DVD 48

for

The Federation of Oils, Seeds and Fats Associations Ltd

by

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DVD 48

July 1995

THE DETERMINATION OF SULFUR IN
ANIMAL AND VEGETABLE OILS
I. LITERATURE SURVEY

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THE INTERNATIONAL
CENTRE FOR INFORMATION,
FOOD SCIENCE AND
TECHNOLOGY

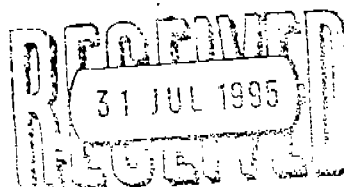


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Mr W N A King
FOSFA International
20 St Dunstan's Hill
London EC3R 8HL



26 July 1995

Dear William

Ref: Project DVD 48: Determination of sulphur in oils

Please find herewith 16 copies of our literature survey on methods for determining sulphur in oils.

I understand that you or the Research Committee wanted a copy of the method used by the Grain Research Laboratory of the Canadian Grain Commission. This is included as an Appendix to the literature survey. I wrote to Dr Jim Daun to ask for his permission to include this method in the survey. He replied, giving his permission, and saying that "As far as I know the method is still used, albeit sporadically, by the Canadian canola industry and is still listed in the specifications for canola oil. I still have an interest in the area and would be willing to work, consult or collaborate with FOSFA on the development of their method."

Yours sincerely

A handwritten signature in cursive script, appearing to read "Margaret".

M V Cooke (Miss)
Analytical Chemistry Section

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29 August 1995

TO: William King
FROM: David Berner
RE: Research Project - Determination of Sulfur

I have discussed the Canadian Grain Commission (CGC) method for sulfur in oils and fats with Jim Daun. The amount of mercury used in the method CGC method is quite small. The laboratories in Canada that use the method isolate the spent mercury via precipitation with hydrogen sulfide. With the isolation of mercury in this manner, there is no problem in the disposal of the remaining laboratory waste. The very small amounts of mercury isolated in this a manner can be stored and eventually disposed of in accordance with local regulations.

The use of mercury in the method would not necessarily preclude its use as far as the AOCS is concerned; however, the AOCS Uniform Methods Committee (UMC) may be reluctant to adopt a new method that uses mercury. I believe it is important to include in the method a note indicating that mercury must be isolated (by precipitation with hydrogen sulfide), stored in a suitable container and disposed of in accordance with local regulations. If those points are included in the method, I believe it will stand a better chance of adoption by the AOCS UMC.

According to Jim Daun, lead is an alternative to mercury, but the environmental and disposal concerns are still present. Jim Daun indicated that one could use a spectrophotometric method, rather than titration with mercuric acetate, however, there are problems associated with the spectrophotometric method - sulfur adheres to the glassware so all of the sulfur may not be quantitated and the method requires some experience to carry it out correctly.

Jim Daun said he would act as a consultant should the FOSFA Research Committee take on the study of the method.

I hope the meeting of the Research Committee goes well; sorry I cannot attend.

Best regards,

A handwritten signature in cursive script that reads "David".

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INTRODUCTION

A Project Proposal for work on methods for determining sulfur in oils was sent to the Federation of Oils, Seeds and Fats Associations Ltd (FOSFA International) in May 1994. Some of the available methods were described in the introduction to the Proposal. It was concluded that the method of the Canadian Grain Commission, which measures the sulfur that will react with, and therefore poison, a Raney nickel catalyst, would probably be the most suitable method to investigate.

Following a discussion of the Project Proposal, the FOSFA Research Committee suggested that it would be desirable to carry out a literature search before any practical work was started, to make sure, as far as possible, that no suitable methods had been overlooked. This report presents the information obtained from the literature, from internal discussions, and from correspondence with known experts.

LITERATURE REVIEWED

Methods given in Project Proposal DVD 48

When Project Proposal DVD48, "The determination of sulphur in animal and vegetable oils", was first prepared and submitted to FOSFA the methods that were already to hand could be divided into two groups, those determining total sulfur, and those measuring the sulfur which will bind to, and therefore poison, a hydrogenation catalyst. These methods, which were given in the Project Proposal, can be summarised as

For total sulfur:

1. ASTM 3246-76, a coulometric method for petroleum products, formerly the FOSFA contractual method.
2. The Wickbold combustion method, which is also a petroleum-industry method.
3. X-ray fluorescence.
4. Inductively coupled plasma-atomic emission spectrophotometry (ICP-AES).

For catalyst-poisoning sulfur:

1. Baltes (1967). The oil is hydrogenated in the presence of a nickel catalyst, and the sulfur binding with the catalyst is liberated as hydrogen sulfide, which is absorbed in alkaline acetone and titrated with mercuric acetate.
2. "Nordic" method, similar in principle to the Baltes method, but using a commercial catalyst.

An IAFMM paper describes a small ring test to compare the Nordic and Baltes methods with two methods of determining total sulfur by oxidation to sulfate.

3. A factory method, based on the Baltes method, but using a Raney nickel catalyst, and without the use of gaseous hydrogen.
4. The Canadian Grain Commission GRL method (Daun). The oil is reacted with Raney nickel, and acidified to liberate hydrogen sulfide, which is absorbed into alkaline acetone, and titrated with mercuric acetate. The method is standardised by running S-containing standards right through the method.

Extended literature survey

When the FOSFA Research Committee considered Project Proposal DVD48 it concluded that a more extensive search of the literature should be carried out before any practical work was commenced, to ensure, as far as possible, that no suitable methods had been overlooked. The Leatherhead Food RA "FROSTI" database was therefore searched for relevant references over the past 20 years. In addition, many references quoted in these papers and other

literature were also traced and examined.

On the database, the majority of the references to sulfur in oils relate to rapeseed oil, with few references to marine oils being found. Much of the work was carried out in Canada, particularly at the Department of Food Science at the University of Guelph, the Canadian Institute of Fisheries Technology at the Technical University of Nova Scotia, and the Grain Research Laboratory of the Canadian Grain Commission in Winnipeg.

The references have been divided into three categories: methods which measure a) total sulfur, b) the sulfur that will combine with (i.e. poison) the hydrogenation catalyst, and c) volatile sulfur.

Methods for Total Sulfur

The problem as regards the interpretation of results for the total sulfur content of oils is that it has been shown by a number of workers that the sulfur in an oil can be present in a number of forms, which have different effects on the flavour of the finished oil and on the performance of any hydrogenation catalyst. Devinet, Biasini & Naudet (1980), for instance, demonstrated that the sulfur compounds in rapeseed oil can occur in volatile, thermolabile and non-volatile forms, and that their relative proportions vary according to the particular stage of the refining process.

A very simple method for total sulfur, attributed to Sosulski (Embong & Jelen, 1977, and Prior, Vadke & Sosulski 1991), consists of reacting the oil with the hydrogen produced by the addition of glacial acetic acid and magnesium turnings to the oil. The liberated hydrogen sulfide is swept from the oil with nitrogen and forms a dark stain on a dry lead acetate paper. The colour of the stain is compared with that from known sulfur standards, over a range equivalent to 5 to 100 ppm of sulfur in the oil. This method does not seem to have been used widely, but might be a simple limit test, even if not fully quantitative. One of the authors of this literature survey doubts whether the method would determine all inorganically bound sulfur, such as sulfate, and therefore the result for total sulfur would be low.

A technique that is widely used is the combustion of the oil with oxygen, either at atmospheric pressure (the Schöniger flask method) or at high pressures in an oxygen bomb. The sulfur oxides so formed are measured as sulfate after absorption in hydrogen peroxide. McGinley (1991) quotes papers by Belisle, Green & Winter (1968), Persmark (1972), and Halvarson & Hoffmann (1980), which describe methods that convert the Schöniger flask procedure into flow-through methods. In the latter the sulfate so formed is titrated with barium ions, using Thorin as indicator. The end-point is detected spectrophotometrically at 525 nm.

Several authors, including Abraham & deMan (1987a) and Vijesundera, Ackman, Abraham & deMan (1988) determine total sulfur by combustion in a Parr oxygen bomb, measuring the resultant sulfate by ion chromatography. Ion chromatography is a more sensitive method for measuring the oxidation products than many that were previously used in conjunction with oxygen flasks or bombs.

Other workers have used inductively coupled plasma atomic emission spectro-

photometry (ICP-AES) to measure total sulfur. According to deClercq, Daun, Loutas, Marianchuk & Moody (1991), the difference between the so-called Raney nickel sulfur, the sulfur which binds with the catalyst, and total sulfur determined by ICP-AES, is less than that quoted by Abraham & deMan (1987a), who measured total sulfur by oxygen bomb combustion, followed by ion chromatography. The authors could not account for the discrepancy, saying that it was possible that the method might not account for all the sulfur in the sample, and that the recovery of sulfur in all oxidation states by ICP-AES should be studied further.

Methods for Catalyst-poisoning Sulfur

Sulfur is the most potent catalyst poison, and for this reason the sulfur content of hydrogenation feedstocks is of the utmost importance. Fortunately, significant amounts are found only in rapeseed and fish oils. Rapeseed sulfur is derived from glucosinolates, while fish oil sulfur originates from amino acids. It is by no means clear whether or not the new forms of low-glucosinolate rapeseed will still give rise to sulfur in the oil, since it is claimed, (Booth, 1994), that sulfur-containing fertiliser is still needed for a profitable rapeseed harvest. Walker (1995) has shown that low-glucosinolate seeds are the result of poor sulfur metabolism in the plant. As a consequence, increased levels of sulfur fertiliser are needed with these new varieties; otherwise, the plants will not thrive.

The various sulfur compounds have differing poisoning effects on catalysts. For example, Abraham & deMan (1987b) found allyl isothiocyanate to be more potent than either heptyl isothiocyanate or 2-phenylethyl isothiocyanate. Earlier, Daun & Hougen (1977) identified four of the seven volatile compounds that they had isolated from rapeseed oil as 5-vinyl-2-oxazolidinethione, butenyl, pentenyl, and phenylethyl isothiocyanate.

Many workers have developed the methods of Granatelli (1959) and Baltés (1967) for measuring the amount of sulfur that will react with a hydrogenation catalyst, as an indication of the potential of the oil to poison the catalyst under commercial conditions. The oil is heated with catalyst, almost always Raney nickel, either in the presence or in the absence of gaseous hydrogen. After this reaction the mixture is acidified to release hydrogen sulfide, which is swept out of the system with a current of nitrogen, and absorbed in alkaline acetone. The sulfide is titrated against standard mercuric acetate solution, with dithizone as indicator. It may be noted that Franke, Goebel & Hollstein (1972) absorb the hydrogen sulfide in a mixture of cadmium sulfate and sodium hydroxide solutions, and quantify the sulfur colorimetrically by reaction with N,N-dimethyl-p-phenylenediamine in acid solution in the presence of ferric ions, to form methylene blue.

In the current climate of limiting, where possible, the use of hazardous materials, it should, perhaps, be noted that mercuric acetate is listed as toxic and an S1 poison (listed in Schedule 1 of the Poisons Rules 1978). It is debatable whether the reagents used by Franke, Goebel and Hollstein (1972), cadmium sulfate (listed as harmful) and N,N-dimethyl-p-phenylenediamine (toxic), are less of a hazard, assuming, of course, that the colorimetric method is as good as the mercuric acetate titration.

deClercq et al (1991) mention that a Raney nickel method has been specified in

a Canadian Standard for canola oil, but in a private communication in 1993 Daun says that there is no real official Canadian method, but that the method in use at the Grain Research Laboratory of the Canadian Grain Commission is based on the Daun and Hougen (1976) method. This includes titration with mercuric acetate solution, but unlike other procedures using this titration to quantify sulfide, the method is standardised by carrying out the complete process on a sulfur compound, dibenzyl disulfide, of known composition. In the other methods, the sulfur content is simply calculated from the accurately-known concentration of mercury in the titrant, with no allowance for recovery. The Grain Research Laboratory's method is given, with Dr Daun's permission, as an Appendix to this literature survey.

As an indication of the difference between the total and the so-called Raney nickel sulfur, deClercq et al (1991) quote mean values of approximately 29, 14 and 8 ppm of total sulfur, determined by ICP-AES, for solvent-extracted, pressed and degummed oils, respectively, as against mean values of approximately 20, 11 and 7 ppm for the Raney nickel sulfur.

Methods for Volatile Sulfur Compounds

Papers by Cho-Ah-Ying & deMan (1989) and Abraham & deMan (1985), among others, describe the determination of sulfur compounds that can be volatilised by heating canola oil at temperatures below 210 °C. The major compounds are isothiocyanates. The compounds have been identified by gas-liquid chromatography, and quantified by infra-red measurements. Abraham & deMan give values for Raney nickel and volatile sulfur, while Cho-Ah-Ying & deMan also quote total sulfur contents.

As isothiocyanates are known to poison hydrogenation catalysts, and must therefore react with nickel, it seems fairly certain that the volatile sulfur compounds are also determined by methods designed to measure nickel-poisoning sulfur, as discussed above. The need for a separate FOSFA method to measure volatile sulfur compounds *per se* is thus not so obvious.

GENERAL DISCUSSION

It is clear that a variety of different sulfur compounds is present in edible oils. The most relevant ones, that is those that cause most trouble to the food industry, are the compounds that poison hydrogenation catalysts, or cause off-flavours. These are essentially the organically bound sulfur compounds, as it is not suspected that inorganic sulfur, in the form of sulfate, would contribute to either of these problems.

Various methods have been reported for the determination of sulfur, but these can give widely differing results, as reported by McGinley (1991), who compiled the following table, which compares results from various methods:

TABLE I

Sulfur determined in rapeseed oils (mg/kg)

Results from	Analytical method				
	Volatiles (GLC)	Raney nickel (Baltes)	Raney nickel (Granatelli) (Daun & Hougen) (modification)	Flask (Oxid'n)	Bomb (Oxid'n)
Halvarson & Hoffmann (1980)	-- -- -- 0.291	2.7 0.2 6.9 --	6.5 2.0 11.3 1.3	12.1 5.0 18.8 --	-- -- -- 17.5
Abraham & deMan (1987a)	0.128 0.322 trace	-- -- --	0.36 1.2 0.2	-- -- --	16.5 15.7 13.6

RECOMMENDATIONS FOR FUTURE WORK

The choice of method for sulfur in oils appears to be between the determination of total sulfur and/or "Raney nickel sulfur". If total sulfur is required, a method based on combustion in an oxygen bomb and determination of sulfate by ion chromatography would seem to be the best. The cost of the bomb, and accessories (Parr Instrument Company, Moline, Illinois, USA), is approximately £2,500. Ion chromatographs, although expensive, are now widely used in analytical laboratories.

If a measure of the sulfur that would poison a catalyst is required, the choice would seem to be the Canadian Grain Commission version of the Daun & Hougen Raney nickel method (see Appendix). According to the illustration in the protocol, the apparatus required appears to be composed of normal laboratory glassware.

The sulfur compounds likely to influence flavour are believed to be those that are organically bound, and probably volatile. As these react with Raney nickel the Canadian method should also satisfy those whose interest relates to flavour, rather than catalyst poisoning.

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SULFUR CONTENT DETERMINATION IN CANOLA/RAPSEED OIL

Method of the Canadian Grain Commission
Grain Research Laboratory

1. SCOPE AND FIELD OF APPLICATION

This test describes a method for the determination of sulfur in canola/rapeseed oil.

2. SAFETY AND HANDLING

2.1 Hazards. (Consult MSDS Centre in Room 1310).

2.1.1 Fire Hazard.

CAUTION: RANEY NICKEL PYROPHORIC WHEN DRY.
Finely divided nickel can ignite in air if allowed to dry.

2.1.2 Hazardous Reactions.

Methanol: Methanol will ignite when poured onto Raney Nickel if traces of air are present.

Organic Solvents: Raney Nickel recovered from methanol, ethanol, pentanol, acetone, benzene, cyclohexane or P-dioxane explodes when heated above 100°C.

2.1.3 Health Hazards.

Nickel may cause dermatitis in sensitive individuals.
Mercuric acetate is highly toxic by ingestion, inhalation and absorption. A strong irritant.
Dibenzyl disulphide is an irritant to eyes and skin.

2.2 Handling and Storage.

Wear rubber gloves laboratory coat and eye protection. When preparing catalysts work in the fumehood. Do not pipette titrant by mouth.

2.3 Waste Disposal.

2.3.1 Disposal of Unused catalyst.

Raney nickel catalyst may be stored safely under 2-propanol for at least 2 weeks. It retains significant activity for much longer periods of time however and if it is allowed to dry and come into contact with air, spontaneous combustion may take place even if the absorbed hydrogen has dissipated. Catalyst should not be stored beyond the end of a given set of experiments. Any catalyst not used at the end of the set of analyses must be destroyed as follows:

The unused catalyst should be transferred to a 250 mL Erlenmeyer flask in a fume hood. Slowly add 20 mL of 60% HCl and allow to digest until all the nickel has dissolved. Hydrogen is generated during this reaction. The solution is slowly basified with sodium hydroxide to precipitate nickel hydroxide. The precipitate is collected and stored for disposal. The aqueous solution is washed down the drain with 50 volumes of water.

- 2.3.2 Disposal of used (spent) catalyst.
After the contents of the reaction flask are cool dispose down the solvent disposal drain in Room 1318. Rinse flask with 2-propanol and seal drain with water.

3. REFERENCES

JAOCS 53:169 (1976)
Merck 6337, 8018

4. DEFINITION

The whole of the organo-sulfur compounds that react with the Raney nickel and are trapped and measured under the operating conditions below.

5. PRINCIPLES

Activated Raney nickel reacts with sulfur in the oil to produce nickel sulfide. The nickel sulfide reacts with strong acid to produce hydrogen sulfide which is trapped in a receiving base. The trapped hydrogen sulfide is titrated with mercuric acetate using dithizone indicator.

6. REAGENTS

- 6.1 Nickel-aluminum alloy, powder (50% Ni, 50% Al); see Section 2 for Safety and Handling.
- 6.2 Sodium hydroxide, 2.5 N; to 800 mL water add 100g NaOH and dilute to 1000 mL.
- 6.3 Sodium hydroxide, 1N; to 800 mL water add 40g NaOH and dilute to 1000 mL.
- 6.4 Hydrochloric acid, 60% (V/V); to 300 mL water add 600 mL HCl and dilute to 1000 mL.
- 6.5 2-Propanol (isopropanol), reagent grade.
- 6.6 2-Propanol (isopropanol), reagent grade; 95% (V/V); to 50 mL water add 950 mL 2-propanol and mix.
- 6.7 Acetone, reagent grade.

6.8 Mercuric acetate, certified; 0.012 M. Place 950 mL water in a 1 L flask, add 3.82 g mercuric acetate, 12.2 mL acetic acid and dilute to 1L. See section 2 for Safety and Handling.

6.8.1 Mercuric acetate, 0.0012 M.
Pipette 10 mL of solution in 6.8 into a 100 mL flask and dilute to 100 mL with water.

6.9 Dithizone (diphenylthiocarbazone), crystal, reagent grade, indicator solution. Place 10 mg of crystals in a 10 mL flask, dissolve in acetone and dilute to the mark with acetone.

6.10 Nitrogen.

6.11 Ice.

6.12 Methyl Isobutyl Ketone (MIBK); Certified.

6.13 Dibenzyl disulfide, reagent grade; 3 mg/mL; place 0.750 g of dibenzyl disulfide into a 250 mL flask and dilute to 250 mL with methyl isobutyl ketone.

7. APPARATUS

Usual laboratory apparatus and in particular:

7.1 Analytical balance.

7.2 Centrifuge and 50 mL centrifuge tubes with screw-caps.

7.3 Water bath.

7.4 Ice bath.

7.5 Pipette, 10 mL, class A.

7.6 Burette, 10 mL with 0.05 mL graduations.

7.7 Disposable pasteur pipettes, glass or plastic.

7.8 Magnetic stirrer.

7.9 Sulfur-digestion apparatus (Fig. 1) including:

7.9.1 Round bottom boiling flask, 125 mL, short neck with a ST (Standard Tapered) joint fitted with a cylindrical filling funnel, 20mL with open top, ST P.T.F.E. metering valve stopcock and a gas inlet tube.

7.9.2 Distilling column, water jacketed, with hooks.

- 7.9.3 Gas dispersion tube with ST outer joints with hooks.
- 7.9.4 Tubing with ground joint ST inner joints with hooks for connecting distilling column and gas dispersion tube.

8. RANEY NICKEL CATALYST PREPARATION

Activated Raney nickel is produced by reaction of nickel-aluminum alloy and strong sodium hydroxide.

- 8.1 Weigh 1 g NiAl alloy into 50 ml centrifuge tube.
- 8.2 Place tubes in an ice bath.
- 8.3 Slowly add 5 ml distilled water per tube and let stand 10 minutes.
- 8.4 Slowly add 10ml of 2.5 N NaOH and allow to react (bubble) 30 minutes.
- 8.5 Cap tubes and place in 50°C bath for 2 hours.
- 8.6 Centrifuge at 1000 rpm for 10 minutes.
- 8.7 Discard supernatant.
- 8.8 Wash catalyst pellet with 2 x 15 ml water and 2 x 15 ml isopropanol, centrifuging between each wash.
- 8.9 Prepared catalysts may be stored under 2-propanol for at least 2 weeks.
- 8.10 See Section 2 for disposal of unused catalyst.

9. PROCEDURE

- 9.1 Preparation of the test sample.
Oil to be used should be free of moisture and solvents.
- 9.2 Test portion.
The test portion shall be representative of the analysis sample and tested in duplicate.
 - 9.2.1 Weigh 15.00 to 20.00 g of oil into reaction (boiling) flask taking care not to get oil on the ground glass joint.
- 9.3 Raney Nickel Reduction of Sulfur Compounds.
 - 9.3.1 Discard the 2-propanol from a stored Ni pellet, add 10ml of 95% 2-propanol, mix, and transfer to reaction flask containing oil.

- 9.3.2 Attach reaction flask to water condenser (Fig. 1), connect N line to reaction flask and adjust flow to 4 p.s.i. through the oil.
- 9.3.3 Place heating mantle under flask.
- 9.3.4 Immerse the bubbler (Fig. 1) in a 250 ml beaker containing 50.0 mL of 1 N. NaOH and stir slowly.
- 9.3.5 Turn on heating mantle and boil for 90 minutes.
- 9.4 Analysis of Sulfur Compounds.
 - 9.4.1 To the beaker containing the bubbler, add 50.0 mL acetone and 0.5 ml indicator solution.
 - 9.4.2 Add 20 ml of 60% HCl into the filling funnel.
 - 9.4.3 Adjust nitrogen flow down (2-3 p.s.i.) and position beaker so stir bar is directly under bubbler for maximum dispersion of bubbles.
 - 9.4.4 Slowly add the HCl to the boiling flask.
 - 9.4.5 Begin titration with .0012 M mercuric acetate (end point change is from bright amber to strawberry red).
 - 9.4.6 Add enough acid to turn solution in boiling flask green.
 - 9.4.7 After addition of HCl let boil another 15 minutes.
 - 9.4.8 Continue titration during the boiling stage.
 - 9.4.9 Rinse the bubbler tube with solution from the beaker. (See Section 11.)
 - 9.4.10 If necessary continue titration and record volume of titrant used to the nearest 0.01 ml.
- 9.5 Titration Reagent Blank.
 - 9.5.1 To a 250 mL beaker add 50.0 mL 1N NaOH and 50.0 mL acetone, mix.
 - 9.5.2 Add 0.5 mL indicator solution and titrate with .0012 M mercuric acetate (endpoint change is from bright amber to strawberry red).
 - 9.5.3 Record volume of titrant used (usually about 0.10 ml).

10. EXPRESSION OF RESULTS

10.1 Method of calculation and formula.

The concentration of sulfur (mg/Kg) in the oil sample is calculated as:

$$(V_s - V_b) \times K / W$$

where V_s is the volume of titrant to the endpoint for the sample.

V_b is the volume of titrant to the endpoint for the blank (usually 0.10 ml).

K is a constant determined from calibration of oil standards (usually expressed as ug S/ml titrant).

W is the weight of oil in grams.

10.2 Calibration.

10.2.1 Preparation of dibenzyl disulfide standard solution.

Weigh 0.750 g of dibenzyl disulfide into a 250 ml volumetric flask, dissolve in MIBK and dilute to the mark.

10.2.2 Preparation of sulfur oil standards.

Weight out 5 x 250.0 g samples of a non-sulfur containing oil (e.g. peanut). Transfer 0.0, 1.0, 2.0, 3.0 and 4.0 ml of the dibenzyl disulfide solution into one of the oil samples. This will provide oil standards containing 0, 3, 6, 9 and 12 ppm S.

10.2.3 Determination of K

The oil standards are analyzed in duplicate to determine K , ug S/ml titrant.

$$K = W \times C / (V_s - V_b)$$

where W is weight in grams of the oil standard

C is the concentration of the oil standard in mg/Kg (ppm)

V_s is the volume in mL of titrant for the standard.

V_b is the volume in mL of titrant for the reagent blank.

11. NOTES ON PROCEDURE

To rinse the bubbler without dismantling the digestion apparatus, switch off heating mantle, stop nitrogen flow, and cool reaction flask contents by rapid fanning and/or immersion in cool water. The solution from the beaker will rise and rinse out the bubbler tube. When the solution nears the top of the vertical tube, switch the N_2 back on to return the solution to the beaker. Flush the tube a second time. Usually the color of the solution returns to amber

during the first rinse. Add more titrant to maintain the endpoint color.

12. REPEATABILITY

A relative standard deviation of $\pm 10\%$ may be expected within a laboratory.

13. TEST REPORT

The test report shall show the method used and the result obtained. It shall also mention any operating conditions not specified in this method, or regarded as optional, as well as circumstances that may have influenced the result.

The report shall include all details required for the complete identification of the sample.

D. R. DeClercq
February, 1989
Amended July 11, 1990

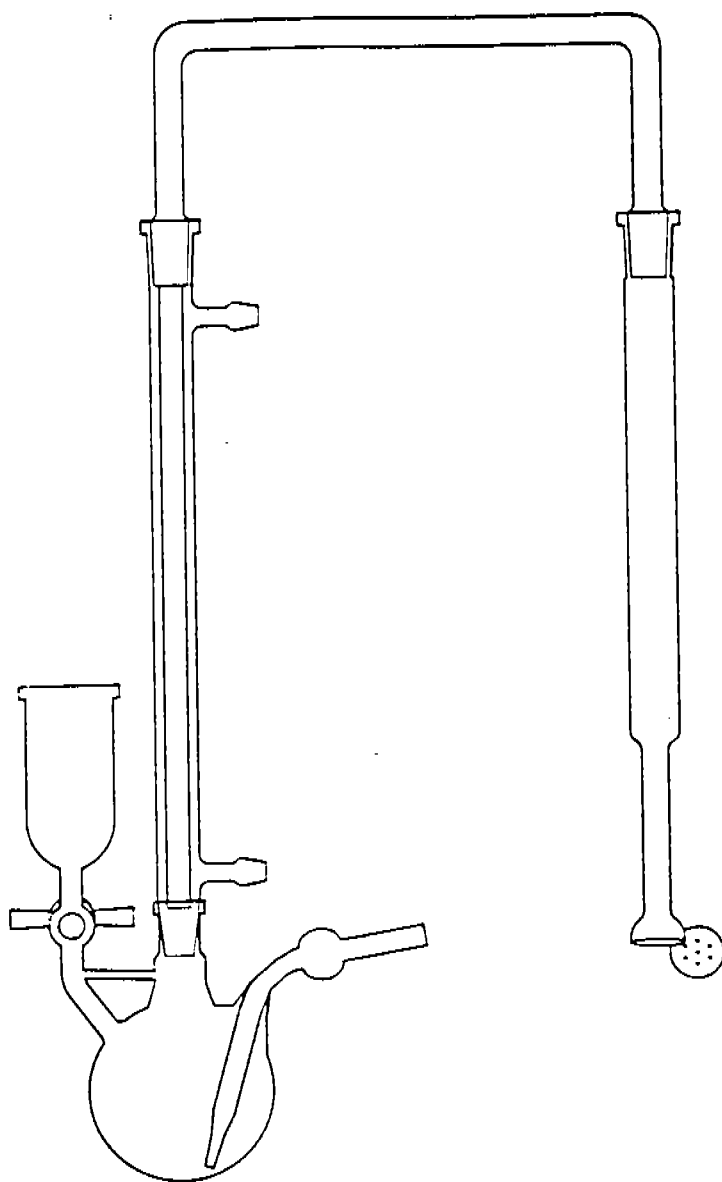


Figure 1 • Raney Nickel Reduction Apparatus