April 17, 1972

Mr. M. Morgan Hoover, Secretary
Food, Drug, and Cosmetic Chemicals Committee
Manufacturing Chemists Association
1825 Connecticut Avenue, N.W.
Washington, D.C. 20009

Re: IUPAC Draft Specs for Dispersion Solvents
Used in Food

Dear Morgan:

Reference your letter of March 29, Allied Chemical is not a prime producer of any of subject solvents, but the writer would suggest that some attempt be made to set standards as uniform as possible throughout the world. To this end, I would recommend that any new set of specifications such as those being prepared for IUPAC fully recognize the existence of prior standards.

It is questioned whether IUPAC needs to establish specifications if specifications from recognized sources already exist. Thus, specifications for food quality propylene glycol have already been set by the Joint FAO/WHO Expert Committee on Food Additives (Seventh Report, 1964) and by Food Chemical Codex. These two specifications for propylene glycol are very similar and, since the Expert Committee report pre-dates the Codex specifications, would guess that the latter was lifted substantially unchanged. There are minor variations such as "residue on ignition" in the Codex specifications and a stricter heavy metals test.

It is noted that Dr. Howard's draft includes specifications for sulfate and chloride, probably derived from U.S.P. specifications for propylene glycol. Since an "ash" or "residue n ignition" test limits these impurities and they are not harmful in food in amounts likely to be present, the writer can see no adequate reason for these specifications. On the other hand, it is necessary that arsenic and heavy metals be limited in food chemicals, even though the likelihood of their being present is remote. The need for refractive index specifications is questioned if other means of identification are given as in FAO/WHO and Codex specifications.

To the writer's knowledge, the only other food chemical on Dr. Howard's list for which a monograph has been written by a public organization is that for glycerol in Food Chemicals Codex. If this is, in fact, true, Dr. Howard is setting a precedent for food additive specifications for the other chemicals listed. In this regard, the writer thinks it preferable to follow the pattern in FAO/WHO or Food Chemicals Codex, i.e. description, identification and specifications, the latter covering assay, physical property limits, limits for anticipated impurities and limits for common toxic elements (arsenic, lead, other heavy metals) i.e. the minimum of specifications which will reasonably guarantee healthfulness.

Unfortunately, I do not have the time to investigate the proposed specifications and methods more thoroughly, but do think that international uniformity should be an objective.

Very truly yours,

W. A. Knapp
Consultant-Toxicology

WAK:pb

cc: Mr. T. W. Hanavan
E. I. dePont de Nemours & Company
1007 Market Street
Wilmington, Delaware 19898

MANUFACTURING CHEMISTS ASSOCIATION
1872 A CENTURY OF SERVICE 1972
1825 CONNECTICUT AVENUE, N.W. WASHINGTON, D.C. 20009 (202) 483-6126

March 29, 1972

To: FOOD, DRUG, AND COSMETIC CHEMICALS COMMITTEE

Subject: IUPAC Draft Specs for Dispersion Solvents Used in Food

Gentlemen:

Dr. Hartley Howard, Technical Director of Borden Inc., has been delegated to solicit comments on the attached proposed specifications from U. S. industry. Accordingly he has requested the assistance of MCA, as well as GMA and FEMA.

Please let me have any comments you may have on these by May 10, so that they may be forwarded to Dr. Howard in time to be received by May 15, the date he needs them.

Thank you.

Sincerely yours,

M. M. Hoover, Secretary
Food, Drug, and Cosmetic
Chemicals Committee

MMH:gr

Attachment

Distribution "B"
Food Additives Contacts in MCA Member Companies

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

APPLIED CHEMISTRY DIVISION

FOOD SECTION

DRAFT SPECIFICATIONS FOR SOME 7 DISPERSION SOLVENTS USED IN FOOD

Food Additives Commission

Feb. 1972

CONTENTS

DRAFT SPECIFICATIONS FOR SOME 8 DISPERSION SOLVENTS USED IN FOOD

1. Preamble

In 1970 the Food Additives and Contaminants Commission of the Food Section of IUPAC drew up minimum specifications as for 7 extraction solvents used in Food Processing. In the course of this work specifications were obtained for many other solvents and it was thought worthwhile to extend the study to dispersion solvents and in particular, ethanol, propan-2-ol, glycerol, glycerol monacetate, glycerol diacetate, glycerol triacetate, propan-1,2-diol and butan-1,2-diol.

2. Minimum specifications

In compliance with the general recommendations of the FAO/WHO no solvent for use in food should be used which contains more than 0.001% of heavy metal expressed as lead and not more than 0.0003% arsenic. The limiting quantities are expressed as % w/v throughout except where indicated.

All temperatures are in degrees centigrade.

2.1 Ethanol

		Method
Assay, not less than	95% v/v	
Relative Density 20°/20°	0.812-0.814	1
Residue at 100°, not more than	0.002%	2
Free Acidity (as acetic acid), not more than	0.005%	3
Methanol	Passes Test	4
Aldehydes and Ketones (as acetone), not more than	0.02%	5
Coloration of residue with sulfuric acid (fusel oil)	Passes Test	6
Fujiwara Test	Negative	7

Note:

Other grades with higher water contents can be used, depending on the technological requirements; the specifications for these should be as above with suitable adjustment for any extra water present.

2.2 Propan-2-ol

		Method
Assay, not less than	99.5% v/v	
Relative Density 20°/20°	0.785 - 0.788	1
Distillation range, 100%	81.0° - 83.0°	8
Water, not more than	0.3%	9
Residue at 100°, not more than	0.002%	2
Free acidity (as acetic acid) not more than	0.005%	3
Aldehydes and ketones (as acetone) not more than	0.1%	5
Coloration of non-volatile residue with sulfuric acid	Passes Test	6
Fujiwara Test	Negative	7

2.3 Glycerol

		Method
Assay, not less than	99.0%	
Specific Gravity at 15.5°, not less than	1.2627	1
Acidity	Passes test	10
Sulfated ash, not more than	0.01%	11
Iron, not more than	0.5ppm	13
Chloride	Passes test	14
Fatty acids and esters, not equivalent to more than	0.020% as Na_2O	15
Acrolein	Passes test	16

Note:

Other grades with higher water contents can be used, depending on the technological requirements, the specifications for these should be as above with suitable adjustment for any extra water present.

2.4 Glycerol monoacetate

Boiling Point at 165mm Hg	158°	
Relative Density, $20^{\circ}/20^{\circ}$	1.206	8
Refractive Index, $n_D^{20^{\circ}}$	1.452	17
Ash, not more than	0.02%	18
Acidity (as acetic acid), not more than	0.3%	3
Chloride, (as Cl) not more than	0.05% as Cl	14
Sulfate, (as SO_4) not more than	0.05% as SO_4	19

2.5 Glycerol diacetate

Refractive Index $n_D^{20^{\circ}}$	1.439	17
Relative Density at $20^{\circ}/20^{\circ}$	1.180 - 1.195	1
Ash, not more than	0.02%	18
Ester content (as glycerol diacetate)	85 - 95% w/w	21
Water and glycerol	Passes test	22
Sulfate, as (SO_4) not more than	0.05% as SO_4	19
Chlorides, (as Cl) not more than	0.05% as Cl	20
Acidity (as acetic acid), not more than	0.3%	3

2.6 Glycerol triacetate

Relative Density $20/20^{\circ}$	1.156 - 1.166	1
Refractive Index $n_D^{20^{\circ}}$	1.430 - 1.434	17
Water, not more than	0.2% w/w	9
Ash, not more than	0.02% w/w	18
Total acidity (as acetic acid), not more than	0.05%	3
Ester Content (as $(CH_3CO)_3C_3H_5$	98 - 100%	2

2.7 Propan-1,2-diol

		Method
Distillation Range, 100%	185° - 189°	
Relative Density 20°/20°	1.038 - 1.040	1
Distillation range 95% v/v	185° - 189°	8
Refractive Index, $n_D^{20°}$	1.431 - 1.433	17
Ash, not more than	0.005%	18
Acidity (as acetic acid), not more than	0.003%	3
Sulfate as SO_4, not more than	0.001%	19
Chloride as Cl, not more than	0.001%	20

3.1. The determination of specific gravity of solvent

For the purposes of this method the following definition applies. The specific gravity at 20/20°C in air of the glycerol is the ratio of the weight in air of a given volume of the glycerol at 20°C to that of the same volume of water at that temperature the weighing being made with weights adjusted to balance brass weights in air.

1. Apparatus: Density bottle, not less than 25ml capacity, complying with B.S. 733, or Pycnometer of similar capacity.

2. Procedure: Calibrate the specific gravity bottle or pycnometer as follows:

Weigh the clean dry bottle or pycnometer, then fill it with cooled distilled water at about 10°C and maintain it in a bath of water at 20°C until it reaches that temperature. If a bottle is used, insert the stopper in such a way that the capillary is completely filled with water, and then maintain the filled bottle at 20°C until no further alteration in volume occurs. Wipe the stopper. If a pycnometer is used, adjust the volume of liquid to the fixed mark. Remove the bottle or pycnometer from the bath, dry the outside allow to stand in a tared dish for a short time and weigh.

Empty and dry the bottle or pycnometer. Fill it with the sample previously cooled to about 5°C below the temperature of 20°C, making sure no air bubbles are present. Maintain the bottle or pycnometer in a bath adjusted to 20°C until it has reached that temperature. If a bottle is used, insert the stopper in such a way that the capillary is completely filled with glycerol and then maintain at 20°C until no further alteration in volume occurs. Wipe the stopper. If a pycnometer is used, adjust the volume to the fixed mark. Remove the apparatus from the bath, dry the outside, allow to stand for a short time in the tared dish and weigh. Make all weighings in air with weights adjusted to balance brass weights in air.

3. Calculations and results

$$\text{Specific gravity of the solvent at } 20/20^{\circ}\text{C in air} = \frac{W_1}{W_2}$$

where W_1 = weight, in grammes, of glycerol obtained in the test and W_2 = weight, in grammes, of water obtained in the calibration test.

4. Reference British Standard Specification 2621-5: 1964.

METHOD 2

3.2. The determination of non-volatile residues in ethanol and propan-2-ol

1 Principle of method: Evaporation to dryness.

2 Apparatus: A weighed basin of platinum, silica or boro-silicate glass; a boiling water bath; an oven at a temperature $100 \pm 2^{\circ}C$; a desiccator; a balance.

3 Procedure: Evaporate 100 ml of the sample to dryness in a weighed basin on a boiling water bath. Dry the residue for 30 minutes in an oven at a temperature of $100 \pm 2^{\circ}C$. Cool in a desiccator and weigh.

4 Calculations and results: Residue on evaporation (weighed in grams) represents per cent by weight per volume.

5 Reference: British Standard Specification 509: 1964.

METHOD 3

3.3 The determination of the acidity of ethanol, propan-2-ol and acetone

1 Principle of method: Titration against standard base.

2 Apparatus: Microburette, 500 ml conical flask.

3 Reagents: The reagents used shall be of a recognised analytical reagent quality. Distilled water, or water of at least equal purity, shall be used throughout.

(a) Sodium hydroxide 0.1N solution

(b) Phenolphthalein indicator. Dissolve 0.5g of phenolphthalein in 100 ml ethanol (95%) and make faintly pink by the addition of dilute sodium hydroxide solution.

4 Procedure: Place 100 ml of water and a few clean antibumping granules into a 500 ml conical flask of boro-silicate glass and boil for 5 minutes to eliminate carbon dioxide. Cool slightly and add 100 ml of the sample. Boil gently for a further 5 minutes. At the end of this period close the neck of the flask with a stopper carrying a soda-lime tube and allow to cool. When cold remove the stopper, add 0.5 ml of the phenolphthalein indicator and titrate with the sodium hydroxide solution using a microburette.

5 Calculation and results: The acidity, calculated as acetic acid,

$$= \frac{6 \times T}{1000} \% \text{ w/v}$$

where T = volume, in ml., of 0.1N sodium hydroxide solution used.

6 Reference: British Standard Specification 509: 1964.

METHOD 4

3.4. The detection of methanol in ethanol

1 Principle of method Oxidation of methanol by permanganate followed by reaction with fuchsin bisulfite solution

2 Reagents: Potassium permanganate and phosphoric acid solution: dissolve 3g of potassium permanganate in a mixture of 15 ml phosphoric acid (89%) and 70 ml of water; add sufficient water to produce 100 ml.

Oxalic acid and sulfuric acid solution: a 5% w/v solution of oxalic acid in a cooled mixture of equal volumes of sulfuric acid (98%) and water.

Fuchsin bisulfite solution dissolve 1g of basic magenta in 600 ml of water and cool in ice: add 20g of sodium sulphite dissolved in 100 ml of water, cool in ice and add, slowly and with constant stirring, 10 ml of hydrochloric acid; dilute to 1000 ml. If the solution is turbid it is filtered and if brown sufficient decolorising charcoal is added to render it colourless and it is then filtered immediately. Store protected from light.

3 Procedure: Dilute 0.5 ml with water to 5 ml, add 2.0 ml of potassium permanganate and phosphoric acid solution, allow to stand for ten minutes and add 2.0 ml of oxalic acid and sulfuric acid solution; to the colourless solution add 5 ml of fuchsin bisulfite solution allow to stand at a temperature between 15°C and 30°C and examine after 30 minutes. No colour should be produced.

4 Reference: British Pharmacopoeia 1968 p. 24.

METHOD 5

3.5. The determination of aldehydes and ketones in ethanol and propan-2-ol

1 Principle of method: Hydrochloric acid is liberated by the reaction between hydroxylamine chloride and any aldehyde or ketone. The liberated acid is titrated with standard base.

2 Reagents: Hydroxylamine chloride solution
Dissolve 1g of hydroxylamine chloride in 50 ml water, add 50 ml ethanol (95% v/v), and 1 ml bromophenol blue solution followed by 0.1 N sodium hydroxide until the solution becomes green.
0.1 N Sodium hydroxide solution
Bromophenol blue solution: Warm 0.1g of bromophenol blue with 3.0 ml of 0.05 N sodium hydroxide and 5 ml of ethanol (90% v/v) after solution is effected, add sufficient ethanol (20%) to give a total volume of 280 ml.

3 Procedure: Heat 100 ml of hydroxylamine chloride solution in a loosely stoppered flask on a water-bath for 30 minutes, cool, and, if necessary, add sufficient 0.1 N sodium hydroxide to restore the green colour. To 50 ml of this solution add 10 ml of water and 10 ml of the sample and heat on a water bath for ten minutes in a loosely stoppered flask. Cool, transfer to a Nessler cylinder and titrate with 0.1 N sodium hydroxide until the colour matches that of the remainder of the hydroxylamine chloride solution contained in a similar cylinder, both solutions being viewed down the axis of the cylinder.

4 Calculations and results: Aldehydes and ketones, calculated as acetone % v/v

$$= 0.00928T$$

where T = volume in ml of 0.1 N sodium hydroxide used.

5 Reference: British Pharmacopoeia 1968 p.24.

METHOD 6

3.6. The detection of fusel oil in ethanol and propan-2-ol

1 Principle of method: Reaction of concentrated sulfuric acid and fusel oil to give a brown colour.
2 Apparatus: Porcelain dish.
3 Reagents: Concentrated sulfuric acid.
4 Procedure: Allow 25 ml of ethanol or propan-2-ol to evaporate spontaneously in a porcelain dish, protected from dust, until the surface on the dish is barely moist; add 1 ml of sulfuric acid. No red or brown colour should be produced.
5 Reference: British Pharmacopoeia 1968 p.24.

METHOD 7

3.7. Fujiwara test for the detection of polyhalogenate contaminants

1 Principle of method: Reaction of certain polyhalogenated compounds containing the group CX_3 and CHX_2 such as trichloroethylene with pyridine-sodium hydroxide to give a pink or red colour with heat.
2 Apparatus: Constant temperature water bath 70° C, reaction cylinders (Glass stoppered Pyrex 25 ml cylinders).
3 Reagents: Pyridine and sodium hydroxide solution
To 40 ml distilled H_2O add 0.48 ml 15% NaOH.
Add 100 ml colourless pyridine, obtained by distilling technical grade over KOH. Do not store for more than 4 days.
4 Procedure: Take 5 ml of the solvent, add 10 ml Fujiwara reagent, stopper and mix. Remove stopper, place in constant temperature bath at 70°C for exactly 15 minutes, maintaining water level above levels in cylinder. After 15 minutes remove cylinder and place in water bath at room temperature for 5 minutes. Add distilled H_2O to make 16 ml, stopper and mix. Prepare a control using 5 ml distilled water. There should not be a more intense colour in the test than in the control.
5 Remarks: Not all polyhalogenated compounds react.
6 Reference: Feigl Spot Tests in Organic Analysis.

ANNEX 6

3.8. The determination of the distillation range of propan-2-ol, and propan-1,2-diol

1 Principle of method: A 100 ml sample of the solvent is fractionally distilled and the boiling and the dry points recorded.

2 Apparatus: Distillation flask 100 ml.
Thermometer 0-105°C.
Condenser.
Draught screen and asbestos board.

3 Procedure: Assemble the apparatus as described in BS 658. Measure 100 ml of sample into the distillation flask from a graduated measuring cylinder and add a few anti-bumping granules. Place the flask, thermometer and a suitable receiver in position and ensure that the condenser has a steady supply of water. Adjust the rate of heating so that the first drop of distillate falls from the end of the condenser in 5 to 10 minutes. Read the temperature at the instant the first drop falls from the end of the condenser and record as the observed initial boiling point.
Further adjust the rate of heating so that the distillate is collected at the rate of 3 ml per minute. Read the temperature indicated at the instant the last drop of liquid evaporates from the lowest point in the distillation flask and record as the observed dry point. Disregard any liquid on the side of the flask.

4 Interpretation of results: The initial boiling point at 760 mm must not be below that required and the dry point at 760 mm pressure must not be above that specified.

5 Remarks: 1. If the thermometer gives incorrect readings at the observed initial boiling point or observed dry point, correct the readings by subtracting the amount of the error.

2. Read the barometer and apply the corrections as described in BS 658.

3. When the corrected barometric pressure deviates from 760 mm Hg apply further corrections to the observed temperatures by subtracting 0.033°C for propan-2-ol for each millimetre above 760 mm or adding 0.033°C for propan-2-ol for each millimetre below 760 mm.

6 Reference: British Standard Specifications 658, 1595, 509 available from the
British Standards Institution,
British Standards House,
2 Park Street,
LONDON, W1X 4AA,
U.K.

3.9. The determination of water in ethanol propan-2-ol, propan-1,2-diol and glycerol (glycerite)

Water determination by the Karl Fischer method is based upon the fact that water reacts with iodine and sulfur dioxide stoichiometrically in the presence of methanol and pyridine as shown in the following formula

$$H_2O + I_2 + SO_2 + 3C_5H_5N \text{ --- } 2(C_5H_5N^+H)I^- + C_5H_5N.SO_3$$

$$C_5H_5N.SO_3 + CH_3OH \text{ --- } (C_5H_5N^+H)\,O^-SO_2.O\,CH_3$$

Apparatus: Generally, the apparatus comprises two automatic burettes, a titration flask and a stirrer. If necessary, an electrometric device is used for the end-point determination. As the Karl Fischer reagent is extremely hygroscopic, the apparatus should be closed tightly to protect from atmospheric moisture. Desiccants such as silica gel or calcium chloride granules are used for protecting from moisture.

Reagents:

Methanol for Karl Fischer Method: To 1,000 ml of methanol, add 5 g of magnesium powder and heat the mixture in a flask connected with a reflux condenser, at the top of which a calcium chloride tube is attached. If necessary, add 0.1 g of mercuric chloride to accelerate the reaction. When the generation of gas has stopped, distil methanol while protecting from moisture. The water content of methanol must not exceed 0.5 mg per ml. Store with protection from moisture.

Pyridine for Karl Fischer Method: To pyridine, add potassium hydroxide or barium oxide, stopper tightly and allow to stand for a few days. Distil off pyridine and store with protection from moisture. The water content of pyridine must not exceed 1 mg per ml.

Karl Fischer reagent:

Preparation: Dissolve 63g of iodine in 100 ml of "pyridine for Karl Fischer Method", cool in ice and pass dry sulfur dioxide through the solution until the increase of the weight of the solution is 32.3g. Dilute with "methanol for Karl Fischer method" to 500 ml and allow to stand for more than 24 hours. Since this solution deteriorates continuously it should be standardised before use. Protect from light and moisture and store in the cold place.

Standardization of the Karl Fischer Reagent:

Primary Method: Place about 35 ml of methanol in the titration vessel and titrate with the Karl Fischer Reagent to the characteristic end-point. Quickly add about 200 mg of sodium tartrate dihydrate, accurately weighed, and while stirring vigorously, again titrate, to the end-point. The water equivalence factor, f, in mg of water per ml of reagent, is represented by the formula 0.1566 W/V, in which W is the weight in mg of the sodium tartrate dihydrate, and V is the volume in ml of the reagent consumed in the second titration.

Water-Methanol Standard Solution

Preparation: Place 500 ml of "Methanol for Karl Fischer Method" in a dried 1,000 ml measuring flask, and add 2 ml of water, accurately measured. Dilute with "Methanol for Karl Fischer Method" to 1,000 ml. The standardization of the solution should be followed by that of the Karl Fischer reagent. Protect from light and moisture and store in the cold place with the temperature kept relatively constant.

Standardization: Place 20 ml of Water-Methanol Standard Solution measured accurately into a titration flask and titrate with the Karl Fischer reagent to the point at which the colour of the solution just changes from brownish yellow to reddish brown as directed under Procedure. The water content, f^1, in mg per ml of Water Methanol Standard Solution is given by the following formula:

$$f^1 = \frac{f \times \begin{pmatrix}\text{ml of Karl Fischer reagent}\\ \text{consumed in the titration}\end{pmatrix}}{\begin{pmatrix}\text{ml of Water-Methanol}\\ \text{Standard Solution}\end{pmatrix}} -$$

Procedure: The titration with the Karl Fischer reagent should be performed at the same temperature as that used in the standardization. The titration with Karl Fischer reagent may be performed by any of the following methods, unless otherwise specified. In electrometrical determinations, usually a back titration gives a better result. In colorless solutions, the end point of the titration may be determined visually as the point at which the colour of the solution changes from brownish yellow to reddish brown colour(vice versa in the case of a back titration). In coloured solutions, the end point is determined electrometrically by the dead stop method.

For electrometrical determination, immerse two platinum electrodes in the solution to be titrated and pass a definite current (5 to 10 microamperes) by manipulating the variable resistance of the circuit. Add Karl Fischer reagent dropwise with the titration proceeding, the needle of the microammeter will swing noticeably, but will return to the original position within a few seconds. At the end point of the titration, a slight excess of the reagent will increase the flow of current (50 to 150 microamperes) for 30 seconds or longer. In back titration, the needle of the microammeter will scale out when an excess of Karl Fischer reagent is present, and will return rapidly to the original position when the titration attains the end point. The apparatus utilizing a magic eye (electron-ray tube) may be employed instead of a microammeter.

Since f for the Karl Fischer reagent decreases continuously, it may be obtained by titration of 20 ml of Water-Methanol Standard Solution measured accurately as directed under Standardization of Water-Methanol Standard Solution and by calculating by the following formula:

$$f'' = \frac{f^1 \times \text{ml of Water Methanol Standard Solution}}{\text{ml of Karl Fischer reagent consumed in the titration}}$$

Determination of Water in Sample

Place about 25 ml of the solvent in the titration vessel and titrate with the Karl Fischer Reagent to the end-point.

Calculation

The water content of the sample, in mg, is obtained by multiplying the volume of the reagent used in titrating the sample by the coulometric factor, f'', of the reagent.

References

Food Chemicals Codex 1966; Japanese Standards of Food Additives, 1970.

METHOD 10

3.10 The detection of free acidity in glycerol

1. Principle of method: Colour change with methyl orange.
2. Reagents: Methyl orange indicator - dissolve 0.5g of methyl orange in one litre of distilled water.
3. Procedure: To 50 ml of freshly boiled and cooled distilled water add 4 drops (approx 0.2ml) of the methyl orange indicator, and adjust to the neutral colour of the indicator.

To 25 ml of the neutralized water add 25 ml of the sample and shake vigorously for 5 seconds. Allow the layers to separate and note any change in the colour of the aqueous layer when compared with that of the neutralized water. A change of colour towards red indicates the presence of acid.
4. Calculations and results: There should be no acidity to methyl orange.
5. Reference: British Standard specification 1997: 1962.

METHOD 11

3.11. The determination of sulfated ash

1. Principle of method

2. Reagents: sulfuric acid - contains not less than 97% w/w of H_2SO_4.

3. Procedure: Heat 50 g until it ignites and allow to burn. Cool the residue, moisten with sulfuric acid, and ignite.

4. Calculation and results: The residue should not weigh more than that specified.

5. Reference: British Pharmacopoeia 1968 p.444.

METHOD 12

3.12. The detection of copper in glycerol

1. Principle of method: Precipitation as copper sulphide.

2. Reagents: The reagents shall be of a recognized analytical reagent quality. Distilled water or water of at least equal purity shall be used.

   Hydrogen sulphide, saturated solution in water, freshly prepared.

   Hydrochloric acid, 3N solution.

3. Procedure: Mix 10 ml of the sample with 30 ml of water, 1 ml of the hydrochloric acid did 10 ml of the hydrogen sulphide solution. Report whether or not any colour is produced.

4. Calculations and results: There should be no colour produced.

5. Reference: British Pharmacoepia 1963.

METHOD 13

13.13 The detection of iron in glycerol

This method is based on that recommended in the British Pharmacoepia, 1963.

1. Principle of method: Colour reaction with thioglycolic acid

2. Reagents: The reagents used shall be of a recognized analytical reagent quality. Distilled water or water of at least equal purity shall be used.

Thioglycolic acid 90%

Take care not to allow concentrated thioglycolic acid to come into contact with the skin, as it causes painful wounds.

Ammonia solution d = 0.880.

Hydrochloric acid, concentrated d = 1.18

Citric acid 20% solution (w/v)

Standard iron solution - Dissolve 0.173g of ammonium ferric sulphate in 100 ml of water. Add 10ml of the hydrochloric acid and dilute to 1000 ml. This solution contains 0.02 mg of iron in 1 ml.

Dilute 100 ml of this solution to 1000 ml to form the standard solution containing 0.002mg of iron in 1 ml.

3. Apparatus - One-mark volumetric flasks of capacities 100ml and 1000 ml to B.S. 1792.

Nessler cylinders of capacities 50 ml to B.S. 612.

4. Procedure: Weigh 20g of the material to the nearest 0.01g, into a Nessler cylinder. Add 2 ml of the citric acid solution and 2 drops of the thioglycolic acid. Make alkaline with the ammonia solution, dilute with water to 50 ml and allow to stand for 5 minutes.

At the same time, in another Nessler cylinder, mix 5 ml of the standard iron solution with 40ml of water. Add 2ml of the citric acid solution and 2 drops of the thioglycolic acid, make alkaline with the ammonia solution. Dilute to 50 ml with water and allow to stand for 5 minutes. Compare the depths of colour of solution in the cylinders.

5. Calculation and results: There should not be more than 0.5ppm iron content, calculated Fe.

6. References: British Standard Specification 2621-5: 1964.

METHOD 14

3.14. The detection of chloride in glycerol

1. Principle of method: Estimation as Silver chloride.

2. Reagents: The reagents shall be of a recognized analytical reagent quality. Distilled water or water of at least equal purity shall be used.

Nitric acid, dilute solution. Dilute 10.5ml nitric acid, d = 1.42, to 100 ml with water.

Silver nitrate 0.1N solution

3. Procedure: Dilute 10 ml of the glycerol to 100 ml with water. Place 10 ml of this solution in a boiling tube, add 0.25ml of the nitric acid solution, 0.5 ml of the silver nitrate solution and mix. Report whether any turbidity is produced.

4. Calculations and results There should be no turbidity produced.

5. Reference British Standard Specification 2621-5: 1964.

METHOD 15

3.15. The determination of fatty acids and esters in glycerol

1. Principle of method Titration against standard base.

2. Reagents The reagents used shall be of a recognized analytical reagent quality. Distilled water or water of at least equal purity and free from carbon dioxide shall be used.

Sodium hydroxide 0.25N solution.

Sulfuric acid 0.25N solution.

Phenolphthalein indicator 0.5% ethanolic solution, prepared by dissolving 1g of phenolphthalein in 200ml of 95% (v/v) ethanol, and adding 0.5N sodium hydroxide solution cautiously until a faint pink colour persists.

3. Procedure Weigh 50g of the well mixed sample into a 500ml round-bottomed flask. Add 100ml of hot, carbon dioxide - free water and 1ml of phenolphthalein indicator. If the solution is alkaline, adjust to neutrality with the sulfuric acid solution.

Add from a burette 15 ml of the sodium hydroxide solution, connect the flask to a reflux condenser and heat to boiling. Boil for five minutes, allow to cool somewhat and wash down the condenser with a little water. Disconnect the flask, close it with a stopper carrying a soda-lime tube, and cool. Titrate with the sulfuric acid solution.

Carry out a blank test at the same time, but using 140 ml of the water.

4. Calculation and results Fatty acids and esters, per cent as Na_2O equivalent

$$= \frac{0.775\ (T_2 - T_1)}{W}$$

where T_2 = volume, in millilitres, of 0.25N sulfuric acid required for blank.

T_1 = volume, in millilitres, of 0.25N sulfuric acid required for sample.

and W = weight, in grams, of sample taken.

5. References British Standard Specification. 2621-5: 1964.

METHOD 16

3.16. The detection of acrolein in glycerol

Principle of method Reaction of acrolein with sodium nitroprusside to give a blue to green colour in the presence of piperidine.

Reagents Piperidine solution A 1 in 5 solution of piperidine in water.

Sodium nitroprusside solution Dissolve 1g sodium nitroprusside in sufficient water to make 20 ml. Prepare fresh before use.

Procedure Add 1 drop of glycerol on a filter paper previously moistened with one drop piperidine solution and one drop sodium nitroprusside solution.

Results No blue to indigo blue to green colour is produced.

Reference The Japanese Standards of Food Additives 2nd Ed 1970 p.271.

METHOD 17

3.17. The measurement of Refractive Index

The refractive index of any substance is the ratio of the velocity of light in vacuum to the velocity in the substance. It is equal to the ratio of the sine of the angle of incidence to the sine of the angle of refraction. In general, it varies with the wavelength of the light, and also with the temperature.

In these standards, the refractive index n_D^t is defined as the refractive index to air measured at the temperature of t^o, using the D line in the sodium spectrum. The refractive index is measured within $\pm$ 0.2° of the specified temperature for each substance.

METHOD 18

3.18. The determination of ash in glycerol mono, di and tri acetates and propan-1,2-diol

1. Principle of Method:

2. Reagents:

3. Procedure: Slowly burn 50 ml of the solvent, in several portions, in a weighed platinum or silica basin, and gently ignite until all carbonaceous matter has disappeared. Cool in a dessicator and weigh.

4. Calculations and results: Calculate the ash as percent by weight of sample. There should not be more than specified by weight of ash.

5. Reference: British Standard Specification 1594: 1950.

METHOD 19

3.19. The determination of sulfate in glycerol mono diacetates

1. Principle of the method: Precipitation as barium sulfate.

2. Reagent: Barium chloride solution A solution containing 10g barium chloride in 100 ml distilled water.

3. Apparatus: Gooch crucible fitted with an asbestos pad.

4. Procedure: Dilute 50 ml of the solvent to 100 ml with distilled water and heat to boiling point. To the hot liquid add 5 ml of a boiling solution of barium chloride drop by drop; continue boiling for a few minutes and set aside a hot plate for at least 4 hours. Wash the precipitate with hot water by decantation pouring the supernatant liquid and washing through a prepared Gooch crucible fitted with an asbestos pad. Transfer the precipitate to the filter and wash it thoroughly with hot water. Finally dry the crucible and ignite it to constant weight.

5. Calculation and results: For the increase in weight of the crucible calculate the sulfates expressed as SO_4, percent by weight of sample.

$$BaSO_4 \times 0.4113 = SO_4$$

6. Reference: British Standard Specification 1594: 1950.

METHOD 20

3.20. The determination of chlorides in glycerol mono and diacetates

Principle of the method: Estimation of chloride as silver chloride.

Reagents glacial acetic acid/analytical grade.potassium chromate solution. A 5% solution in water.

Silver nitrate solution. A 0.1N solution in distilled water

Procedure Dilute 25 ml of the solvent to 100 ml with distilled water. Add 2 ml glacial acetic acid and 1 ml potassium chromate solution and titrate with 0.1N silver nitrate solution until the red coloration is permanent.

Calculations and Results: Calculate the chlorides thus found as chlorine, Cl, percent by weight of sample.

1 ml 0.1N A_3NO_3 = 0.00355g Cl.

Reference British Standard Specification 1594: 1950.

METHOD 19

3.19. The determination of sulfate in glycerol mono diacetates

1. Principle of the method: Precipitation as barium sulfate.

2. Reagent: Barium chloride solution A solution containing 10g barium chloride in 100 ml distilled water.

3. Apparatus: Gooch crucible fitted with an asbestos pad.

4. Procedure: Dilute 50 ml of the solvent to 100 ml with distilled water and heat to boiling point. To the hot liquid add 5 ml of a boiling solution of barium chloride drop by drop; continue boiling for a few minutes and set aside a hot plate for at least 4 hours. Wash the precipitate with hot water by decantation pouring the supernatant liquid and washing through a prepared Gooch crucible fitted with an asbestos pad. Transfer the precipitate to the filter and wash it thoroughly with hot water. Finally dry the crucible and ignite it to constant weight.

5. Calculation and results: For the increase in weight of the crucible calculate the sulfates expressed as SO_4, percent by weight of sample.

$$Ba\,SO_4 \times 0.4115 = SO_4$$

6. Reference: British Standard Specification 1594: 1950.

METHOD 20

3.20. The determination of chlorides in glycerol mono and diacetates

Principle of the method: Estimation of chloride as silver chloride.

Reagents glacial acetic acid/analytical grade. potassium chromate solution. A 5% solution in water.

Silver nitrate solution. A 0.1N solution in distilled water

Procedure Dilute 25 ml of the solvent to 100 ml with distilled water. Add 2 ml glacial acetic acid and 1 ml potassium chromate solution and titrate with 0.1N silver nitrate solution until the red coloration is permanent.

Calculations and Results: Calculate the chlorides thus found as chlorine, Cl, percent by weight of sample.

1 ml 0.1N $AgNO_3$ = 0.00355g Cl.

Reference British Standard Specification 1594: 1950.

METHOD 19

3.19. The determination of sulfate in glycerol mono diacetates

1. Principle of the method: Precipitation as barium sulfate.

2. Reagent: Barium chloride solution A solution containing 10g barium chloride in 100 ml distilled water.

3. Apparatus: Gooch crucible fitted with an asbestos pad.

4. Procedure: Dilute 50 ml of the solvent to 100 ml with distilled water and heat to boiling point. To the hot liquid add 5 ml of a boiling solution of barium chloride drop by drop; continue boiling for a few minutes and set aside a hot plate for at least 4 hours. Wash the precipitate with hot water by decantation pouring the supernatant liquid and washing through a prepared Gooch crucible fitted with an asbestos pad. Transfer the precipitate to the filter and wash it thoroughly with hot water. Finally dry the crucible and ignite it to constant weight.

5. Calculation and results: For the increase in weight of the crucible calculate the sulfates expressed as SO_4, percent by weight of sample.

$$Ba SO_4 \times 0.4115 = SO_4$$

6. Reference: British Standard Specification 1594: 1950.

METHOD 20

3.20. The determination of chlorides in glycerol mono and diacetates

Principle of the method: Estimation of chloride as silver chloride.

Reagents glacial acetic acid/analytical grade.potassium chromate solution. A 5% solution in water.

Silver nitrate solution. A 0.1N solution in distilled water

Procedure Dilute 25 ml of the solvent to 100 ml with distilled water. Add 2 ml glacial acetic acid and 1 ml potassium chromate solution and titrate with 0.1N silver nitrate solution until the red coloration is permanent.

Calculations and Results: Calculate the chlorides thus found as chlorine, Cl, percent by weight of sample.

1 ml 0.1N $AgNO_3$ = 0.00355g Cl.

Reference British Standard Specification 1594: 1950.

METHOD 21

3.21. Method for the determination of ester content of glycerol triacetate and diacetate

1. Principle of method:

2. Reagents: The reagents used shall be of a recognised analytical reagent quality. Distilled water, or water of at least equal purity, shall be used throughout and shall be freshly boiled and cooled.

Potassium hydroxide - approximately N solution in ethanol.
Hydrochloric acid - N solution.

Phenolphthalein indicator - dissolve 0.5g of phenolphthalein in 100 ml of 95% ethanol and make faintly pink by the addition of 0.1N sodium hydroxide solution.

3. Procedure: Using the same pipette, introduce 50 ml of potassium hydroxide solution into each of two dry 250 ml conical flasks with ground-glass joints. Close the flasks with their glass stoppers. By means of a weighing pipette, transfer 2.0 to 2.5g of the sample, weighed to the nearest 0.001g, into one of the flasks.

Attach the flasks to water-cooled reflux condensers with ground-glass joints and heat for one hour in a boiling-water bath. Withdraw the flasks, still carrying their condensers, and immerse them in cold running water. When cool, wash down the inside of each condenser with two 20 ml portions of water. Disconnect the flasks and wash each joint with a further 20 ml of water. Add 0.5 ml of the phenolphthalein indicator and titrate the mixture immediately with the hydrochloric acid until the pink colour is just discharged.

4. Calculation and results:

For glycerol triacetate: Ester content, calculated as glycerol triacetate, $(CH_3\ COO)_3\ C_3H_5$,

$$\text{percent by weight} = \frac{7.27\ (T_1 - T_2)}{W4}$$

For glycerol diacetate: Ester content calculated as glycerol diacetate $(CH_3\ COO)_2\ C_3H_5OH$ percent by weight

$$= \frac{8.8\ (T_1 - T_2)}{W4} - 1.46C$$

C = percent by weight of acetic acid determined in method 4.

where T_3 = volume in millilitres, of N hydrochloric acid solution required by the blank,

T_2 = volume, in millilitres, of N hydrochloric acid solution required by the test sample.

W4 = weight, in grammes, of sample.

The ester content should be the limits specified.

5. References: British Standard Specification 1997: 1962

METHOD 22

3.22. The detection of water and glycerol in glycerol diacetate

Principle of method: Immiscibility of water and glycerol in benzene.

Reagents: Benzene, analytical grade.

Procedure: Mix 50 ml of benzene with 10 ml distilled water and shake vigorously from time to time for 30 minutes. Allow the mixture to separate into two layers. Remove 25ml. of the clear benzene and add it to 10 ml of the glycerol diacetate in a dry glass-stoppered cylinder of about 100ml capacity. Allow to stand for 30 minutes, shake vigorously and examine for opalescence.

Result: There should be no opalescence.

Reference: British Standard Specification 1594: 1950.

in ...l. of water meets the
ıge 765, using 20 mcg. of lead

ml. into a tared 125-ml.
heated at 105° to constant
ness on a steam bath. *Heat*
tant weight, cool in a desicca-

issolve 15 grams of sodium
ml. of bromine, stirring to ef-
)0 ml. with water. Transfer
. glass-stoppered Erlenmeyer
d 10 ml. of a 1 in 5 solution of
nple. Allow to stand for 15
f potassium iodide and 10 ml.
l *N* sodium thiosulfate just to
erform a blank determination
e volume of 0.1 *N* sodium thio-
required for the sample is not

cher Titrimetric Method, page

l-closed containers.
ve.

ISOLE

hole

$I_2CH_2CH_3$

Mol. wt. 150.22

ving a characteristic anise-type
It is soluble in most fixed oils
lycerin and in propylene glycol.

nd 1.5055 at 20°.

d 0.943.

Limits of Impurities

Arsenic (as As). Not more than 3 parts per million (0.0003 per cent).

Heavy metals (as Pb). Not more than 40 parts per million (0.004 per cent).

Lead. Not more than 10 parts per million (0.001 per cent).

TESTS

Refractive index, page 785. Determine with an Abbé or other refractometer of equal or greater accuracy.

Solubility in alcohol. Proceed as directed in the general method, page 746. One ml. dissolves in 5 ml. of 80 per cent alcohol and remains in solution upon further dilution.

Specific gravity. Determine by any reliable method (see page 4).

Arsenic. A *Sample Solution* prepared as directed for organic compounds meets the requirements of the *Arsenic Test*, page 720.

Heavy metals. Prepare and test a 500-mg. sample as directed in *Method II* under the *Heavy Metals Test*, page 763, using 20 mcg. of lead ion (Pb) in the control (*Solution A*).

Lead. A *Sample Solution* prepared as directed for organic compounds meets the requirements of the *Lead Limit Test*, page 772, using 10 mcg. of lead ion (Pb) in the control.

Packaging and storage. Store in tight, full containers in a cool place protected from light.

Functional use in foods. Flavoring agent.

PROPYLENE GLYCOL

1,2-Propanediol; 1,2-Dihydroxypropane; Methyl Glycol

$CH_3.CH(OH).CH_2OH$

$C_3H_8O_2$ Mol. wt. 76.10

DESCRIPTION

A clear, colorless, viscous liquid having a slight, characteristic taste. It is practically odorless. It absorbs moisture when exposed to moist air. It is miscible with water, acetone, and chloroform in all proportions. It is soluble in ether and will dissolve many essential oils, but is immiscible with fixed oils.

IDENTIFICATION

A. Mix 500 mg. with 3.6 grams of triphenylchloromethane and 5 ml. of pyridine, and heat under a reflux condenser on a steam bath for

ml. warm acetone, and stir
Filter, evaporate the filtrate
night in a refrigerator. Filter
m pyridine (three times) and
obtained melt at about 176°

potassium bisulfate. A fruity
heated to dryness, no sharp,

weight, of $C_3H_8O_2$.
189°.
.037.

rts per million (0.0003 per cent).
han 10 parts per million (0.001

n 0.07 per cent.

olumetric flask about 300 mg.,
hing pipet, dilute to volume with
his solution into a 125-ml. Erlen-
dic l, swirl, and let stand for
solution of sodium bicarbonate,
rsenite and 1 ml. of a potassium
id enough sodium bicarbonate so
ll remain undissolved, and titrate
buret and continuing the titration
lank determination (see page 2)
Each ml. of 0.1 *N* iodine is equiva-

100-ml. sample distils completely

my reliable method (see page 4).

alein T.S. to 50 ml. of water, then
the solution remains pink for 30
f the sample, accurately measured,
xide until the original pink color
Not more than 0.2 ml. of 0.1 *N*

Arsenic. A *Sample Solution* prepared as directed for organic compounds meets the requirements of the *Arsenic Test*, page 720.

Heavy metals. A solution of 2 grams in 25 mL of water meets the requirements of the *Heavy Metals Test*, page 763, using 20 mcg. of lead ion (Pb) in the control (*Solution A*).

Residue on ignition, page 786. Heat a 50-gram sample in a tared 100-ml. shallow dish until it ignites, and allow it to burn without further application of heat in a place free from drafts. Cool, moisten the residue with 5 ml. of sulfuric acid, and ignite at about 800° for 15 minutes.

Water. Determine by the *Karl Fischer Titrimetric Method*, page 804.

Packaging and storage. Store in tight containers.

Functional use in foods. Solvent; wetting agent; humectant.

PROPYLENE GLYCOL ALGINATE

Hydroxypropyl Alginate; Algin Derivative

$(C_8H_{14}O_7)_n$ Equiv. wt., *Calculated*, 234.20

DESCRIPTION

The propylene glycol ester of alginic acid (see *Alginic Acid*, page 20) varies in composition according to its degree of esterification and the percentages of free and neutralized carboxyl groups in the molecule. It occurs as a white to yellowish, fibrous or granular powder. It is practically odorless and tasteless. It dissolves in water, in solutions of dilute organic acids, and, depending upon the degree of esterification, in hydroalcoholic mixtures containing up to 60 per cent by weight of alcohol to form stable, viscous colloidal solutions at a pH of 3.

IDENTIFICATION

A. It responds to *Identification Tests, A, B,* and *C* under *Sodium Alginate*, page 600.

B. Transfer 20 ml. of the saponified solution obtained in the determination of *Esterified carboxyl groups* into a 250-ml. Erlenmeyer flask, add 50 ml. of 0.1 *M* periodic acid, swirl, and allow to stand for 30 minutes. Add 2 grams of potassium iodide, titrate with 0.1 *N* sodium thiosulfate to a faint yellow color, and then dilute the mixture to 200 ml. To 10 ml. of this dilution add 5 ml. of hydrochloric acid and 10 ml. of modified Schiff's reagent. A pink color develops in about 20 minutes (formaldehyde). To another 10 ml. of the solution add 1 ml. of a saturated solution of piperazine hydrate and 0.5 ml. of sodium nitroferricyanide T.S. A blue color develops (*acetaldehyde*). *Note:* Oxidation of propylene glycol alginate yields formaldehyde and acetaldehyde.

per cent and not more than the equivalent of
HCl after drying.
Between +23.5° and +25.5°.

re than 3 parts per million (0.0003 per cent).
Not more than 20 parts per million (0.002

parts per million (0.001 per cent).
re than 0.5 per cent.
ot more than 0.25 per cent.

) mg., previously dried at 80° for 4 hours
ml. of water, add bromothymol blue T.S.,
hydroxide. Each ml. of 0.1 *N* sodium
) mg. of $C_5H_9NO_4.HCl$.
After drying at 80° for 4 hours, deter-
hloric acid containing 125 mg. in each ml.
prepared as directed for organic com-
of the *Arsenic Test*, page 720.
l test a 1-gram sample as directed in
ls Test, page 763, using 20 mcg. of lead
A).

ared as directed for organic compounds
d Limit Test, page 772, using 10 mcg. of

y at 80° for 4 hours.
1 gram as directed in the general

in ll-closed, light-resistant con-

bstitute; flavoring agent.

GLYCERIN

Glycerol

$CH_2OH.CHOH.CH_2OH$

$C_3H_8O_3$ Mol. wt. 92.10

DESCRIPTION

A clear, colorless, syrupy liquid, having a sweet taste. It has not more than a slight characteristic odor, which is neither harsh nor disagreeable. It is hygroscopic and its solutions are neutral. Glycerin is miscible with water and with alcohol. It is insoluble in chloroform, in ether, and in fixed and volatile oils.

IDENTIFICATION

Heat a few drops of glycerin in a test tube with about 500 mg. of potassium bisulfate. The characteristic, pungent vapors of acrolein are evolved.

SPECIFICATIONS

Assay. Not less than 95 per cent of $C_3H_8O_3$.

Specific gravity. Not less than 1.249.

Limits of Impurities

Acrolein, glucose, and ammonium compounds. Passes test.

Arsenic (as As). Not more than 3 parts per million (0.0003 per cent).

Butanetriols. Not more than 0.2 per cent.

Chlorinated compounds (as Cl). Not more than 30 parts per million (0.003 per cent).

Color. Passes test.

Fatty acids and esters. Passes test (limit about 0.1 per cent, calculated as butyric acid).

Heavy metals (as Pb). Not more than 5 parts per million (0.0005 per cent).

Readily carbonizable substances. Passes test.

Residue on ignition. Not more than 0.01 per cent.

Assay

Sodium Periodate Solution. Dissolve 60 grams of sodium metaperiodate ($NaIO_4$) in sufficient water containing 120 ml. of 0.1 *N* sulfuric acid to make 1000 ml. Do not heat to dissolve the periodate. If the solution is not clear, filter through a sintered-glass filter. Store the solution in a glass-stoppered, light-resistant container. Test the suitability of this solution as follows: Pipet 10 ml. into a 250-ml. volumetric flask, dilute to volume with water, and mix. To about 550 mg.