MIL-STD-1438A

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MILITARY STANDARD

INDICATORS, ORGANIC, REAGENT GRADE

FSC 6810

DEPARTMENT OF DEFENSE
Washington, DC 20301

Indicators, Organic, Reagent Grade

MIL-STD-1438A

1. This Military Standard is approved for use by all Departments and Agencies of the Department of Defense.

2. Beneficial comments (recommendations, additions, deletions) and any pertinent data which may be of use in improving this document should be addressed to: Commander, US Army Armament Munitions and Chemical Command, Attn: DRSMC-TSC-S (A), Aberdeen Proving Ground, MD 21010, by using the self-addressed Standardization Document Improvement Proposal (DD Form 1426) appearing at the end of this document or by letter.

FOREWORD

This is the first revision of MIL-STD-1438 on indicators, organic, reagent grade.

The format has been changed to classify indicators into five categories dependent on their applications in use.

CONTENTS

TABLES

1. SCOPE

1.1 Coverage. This standard is a presentation of indicators, organic, reagent grade, including ACS grade. This standard does not necessarily include all of the items represented by the title or all those items which are commercially available. It does contain items preferred for use in the selection of organic indicators, reagent grade, for application by the Department of Defense.

1.2 Application. Indicators, organic, reagent grade, are used in quantitative analytical chemistry for volumetric or titrimetric analyses and for the determination of pH values of solutions. In volumetric or titrimetric analysis, a substance is determined quantitatively by titration. Titration is the process of adding a reagent solution (titrant) of known concentration or reacting strength (titer) until all the substance has reacted, at which point an equivalent amount of the titrant has been added. In a visual end-point determination titrant is added until a suitable indicator shows a change in color or fluorescence or light scattering. The difference between the amount of titrant corresponding to the end-point and that corresponding to the equivalence-point represents the titration error, which can be determined experimentally. In ordinary titrations, the indicator is added to the system to be titrated, and the color change is observed in the solution. Such indicators are called internal or inside indicators.

1.3 Classification. Indicators are available for the different types of volumetric methods, and can be classified into five categories as follows:

a. Acid-base indicators for acid-base titrations in clear solutions.

b. Fluorescent acid-base indicators for titrations in strongly colored or turbid solutions.

c. Adsorption indicators for precipitation titrations.

d. Metallochromic indicators for complexometric titrations of metal cations and titration of anions by metal cations.

e. Reduction-oxidation (redox) indicators for reduction-oxidation potential titrations.

2. REFERENCED DOCUMENTS

2.1 Issues of documents. The following documents, of the issue in effect on date of invitation for bids or request for proposal, form a part of this standard to the extent specified herein.

SPECIFICATIONS

FEDERAL

O-C-265 - Chemicals, Analytical, General Specification For
PPP-C-2020 - Chemicals, Liquid, Dry And Paste; Packaging Of

MILITARY

MIL-I-536 - Indicator Solutions, pH Determination
MIL-D-537 - Disk, Color Standard
MIL-D-11318 - p-Dimethylaminobenzalrhodanine, Reagent
MIL-F-11368 - Fluorescein Sodium, Reagent
MIL-B-11722 - Bromophenol Blue Solution; Indicator
MIL-B-11845 - Bromothymol Blue Solution; Indicator
MIL-W-15000 - Water Testing Chemicals, Boiler, Shipboard Use
MIL-M-50075 - Metanil Yellow, Reagent
MIL-I-52701 - Indicator Solution, pH Determination

STANDARDS

FEDERAL

FED-STD-313 - Material Safety Data Sheets, Preparation And The Submission Of

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MIL-STD-12 - Abbreviations For Use On Drawings, And In Specifications, Standards And Technical Documents

PUBLICATIONS

DOD 4145.19-R-1 - Storage And Materials Handling
DOD 4160.21-M - Defense Utilization And Defense Disposal Manual
DOD 6050.5-LR - DOD Hazardous Materials Information System, Hazardous Item Listing

TECHNICAL BULLETINS

TB MED 502 (DLAM 1000.2) - Occupational And Environmental Health Respiratory Protection Program
TB MED 506 - Occupational And Environmental Health Occupational Vision

(Copies of specifications, standards, drawings, and publications required by contractors in connection with specific procurement functions should be obtained from the procuring activity or as directed by the contracting officer.)

2.2 Other publications. The following documents form a part of this standard to the extent specified herein. Unless otherwise indicated, the issue in effect on date of invitation for bids or request for proposal shall apply.

AMERICAN CHEMICAL SOCIETY (ACS)

Reagent Chemicals, American Chemical Society Specifications

(Application for copies should be addressed to the American Chemical Society, 1155 Sixteenth Street, NW, Washington, DC 20036.)

ASTM

ASTM E 380 - Standard For Metric Practice

(Application for copies should be addressed to ASTM, 1916 Race Street, Philadelphia, PA 19103.)

US PHARMACOPEIAL CONVENTION, INCORPORATED

The United States Pharmacopeia
National Formulary

(Application for copies should be addressed to Mack Publishing Company, Easton, PA 18042.)

CODE OF FEDERAL REGULATIONS (CFR)

Title 29 - Department of Labor, Occupational Safety and Health Agency; General Industry Standards and Interpretations
Title 40 - Environmental Protection Agency; Hazardous Waste And Consolidated Permit Regulations
Title 49 - Department Of Transportation; Hazardous Materials Regulations

DEPARTMENT OF HEALTH AND HUMAN SERVICES (DHHS)

DHHS (NIOSH) Publication No. 83-107 - Registry of Toxic Effects of Chemical Substances

(Application for copies should be addressed to the Superintendent of Documents, US Government Printing Office (GPO), Washington, DC 20402.)

NATIONAL FIRE PROTECTION ASSOCIATION (NFPA)

National Fire Codes

(Application for copies should be addressed to National Fire Protection Association, Battery March Park, Quincy, MA 02269.)

Technical society and technical association specifications, standards, and publications are generally available for reference from libraries. They are also distributed among technical groups and using Federal agencies.

3. GLOSSARY

3.1 Definitions.

Acid or Acidic - A general term for compounds which give hydrogen ions (H^+) in aqueous solution.

Base or Basic - A general term for compounds which give hydroxyl ions (OH^-) in aqueous solution.

Chelating Agent - A compound forming a metal ion complex in a ring structure by means of coordinate bonds.

End-point - The point at which some detectable evidence indicates the completion of a reaction in volumetric analysis by titration.

Equivalence-point or stoichiometric point - The point at which chemically equivalent amounts of reagent and the substance titrated have been brought into reaction.

Indicator - An organic substance, usually a dye, which indicates by a change in its color the presence, absence, or concentration of some other substance, or the degree of reaction between two or more other substances.

pH - A numerical measure of the hydrogen ion concentration, indicating the degree of acidity or basicity of a solution. It is expressed as $pH = -\log_{10}[H^+]$, where $[H^+]$ is the concentration of hydrogen ion in moles per liter of solution. At the neutral point in an aqueous solution, pH = 7. At a pH lower than 7, a solution is acidic. At a pH higher than 7, a solution is basic.

Reduction-Oxidation - A chemical reaction in which an element or an atom within a compound gains one or more electrons and is reduced, and in which another element or atom within a compound loses one or more electrons and is oxidized.

Titration - The process in volumetric analysis of measuring the volume of a solution of known concentration needed to react quantitatively with a solution of a weighed or volumetrically measured quantity of material.

3.2 Abbreviations. The use of abbreviations shall be in accordance with MIL-STD-12. Metric system abbreviations and symbols shall be in accordance with ASTM E380.

4. GENERAL REQUIREMENTS

4.1 Packaging data and labeling. All chemicals included in this standard shall be packaged in accordance with Federal Specification PPP-C-2020 and all applicable documents referenced therein. Shipping containers shall be labeled in accordance with current Department of Transportation (DOT) Hazardous Materials Regulations applicable to each chemical.

4.2 Hazardous materials information. DOD 6050.5, DOD Hazardous Materials Information System (HMIS) requires Material Safety Data Sheets (MSDSs) for all hazardous materials used by DOD. The contractual acquisition of a MSDS is accomplished through use of Federal Acquisition Regulation, paragraph 52.223-3, Hazardous Material Identification and Material Safety Data. The MSDS is prepared in accordance with the instructions in FED-STD-313.

4.3 Safety.

4.3.1 Personal protective measures. The necessary respiratory, eye and skin protection to be used when handling chemicals shall be prescribed by the responsible installation industrial hygiene, medical and safety authorities.

4.3.1.1 Respiratory protection. Respirators, approved by the National Institute for Occupational Safety and Health (NIOSH) or the Mine Safety and Health Administration (MSHA) or by particular respirator schedules of the Bureau of Mines (BM) for the compounds being used, may be employed for intermittent exposure or for supplementing other control measures (refer to TB MED 502 or DLAM 1000.2). Ventilation should be adequate to remove hazardous concentrations.

4.3.1.2 Skin protection. Personnel using these compounds shall be provided with and required to use impervious gloves, sleeves, aprons, and boots whenever indicated. Protective creams and ointments commonly known as "barrier creams" may be of value in certain cases. However, barrier creams should not be used to replace protective clothing. Eye lavages and emergency showers should be located where there is a potential for direct contact with harmful chemicals.

4.3.1.3 Face and eye protection. Personnel using these compounds shall be provided with and required to wear chemical splash-proof safety goggles. (Refer to TB MED 506.) In addition, face shields shall be provided and worn over the goggles if splashing could occur.

4.3.1.4 Training. Training should be provided to ensure that employees know potential hazards of the chemicals with which they come in contact and the symptoms of over-exposure as well as how these chemicals affect the body and bodily functions. A person or persons shall be adequately trained to render first aid.

4.3.1.5 Exercises. Participation in exercises should be stressed to demonstrate skills in the use of personal protective equipment and emergency response equipment.

4.3.2 Storage conditions. DOD 4145.19-R-1 describes general storage practices and requirements for hazardous materials in the DOD supply system. Specific requirements provided in the following paragraphs are supplementary in nature and should be observed in consonance with the DOD storage regulations.

4.3.2.1 Flammable, combustible, pyrophoric and ignitable materials. A flammable material is generally any solid, liquid, vapor or gas that ignites easily and burns rapidly. Combustible materials are generally those that are difficult to ignite and burn slowly. The DOT, in Section 173.115, Subpart D, Part 173 of 49CFR, 1982 Revised and as amended, defines a flammable liquid as one having a closed cup flash point below 100°F (37.8°C). A combustible liquid is defined, by DOT in the above reference, as one having a closed cup flash point at or above 100°F (37.8°C) and below 200°F (93.3°C). A pyrophoric liquid is defined, by DOT in the above reference, as one that ignites spontaneously in dry or moist air at or below 130°F (54.5°C). Materials with flash points of 200°F (93.3°C) or higher are not considered to be nonflammable or non-combustible, but are to be considered as burnable. The Environmental Protection Agency (EPA), in section 261.21 Subpart C, Part 261 of 40CFR*, 1982 Revised and as amended, designates the criteria for flammable and combustible materials and oxidizers that exhibit the characteristic of ignitability (I). Liquids with closed cup flash points of less than

*Refers only to materials that have become waste materials.

140°F (60°C) are defined by EPA as ignitable. The autoignition point (temperature) of a substance is generally defined as the minimum temperature required to initiate or cause self-sustained combustion in the absence of a spark or flame. Materials that ignite easily under normal industrial conditions are considered to be dangerous fire hazards. Such materials must be stored in a manner to prevent ignition and combustion. Easily ignitable substances, such as reducing agents, must be kept away from strong oxidizing agents. All containers must be tightly sealed. It is important to provide adequate ventilation in storage areas, and to locate the storage areas of these items away from fire hazards. Ample fire-control equipment must be easily accessible. Storage buildings, rooms and cabinets should comply with provisions of the National Fire Codes. The building should be electrically grounded and signs posted to prevent the lighting of matches or smoking in the area. Flammable storage areas should be equipped with smoke or fire detection equipment.

4.3.2.2 Water-sensitive fire and explosive hazardous materials. These are materials that react on contact with water or steam to ignite or evolve heat or explosive gases. Such materials exhibit the characteristic of reactivity (R) as designated by the EPA in Section 261.23 of the above reference.* These materials must be stored in well-ventilated, cool, dry areas. All containers must be tightly sealed. These materials are a fire hazard in contact with water or moisture; therefore, it is essential that no sprinkler be used. Otherwise, the building should conform to that required for storage of flammable materials. The building must be waterproof, located on high ground, and separated from other storage areas.

4.3.2.3 Incompatible materials. Materials that are chemically incompatible must be segregated in the storage of both serviceable and unserviceable items. The degree of segregation will depend upon DOD 4145.19-R-1 and local supplementary requirements that insure safe storage conditions. Hazardous storage compatibility codes are provided in the HMIS referred to in paragraph 4.2.

4.3.3 Chemical hazardous exposure limits. Chemical hazardous exposure limits for airborne concentrations of substances are obtained from the current TLVs® Threshold Limit Values for Chemical Substances in Workroom Air, adopted by the American Conference of Government Industrial Hygienists (ACGIH); current Occupational Safety and Health Administration (OSHA) Permissible Exposure Limits (PEL), 29 CFR, Section 1910.1000; and NIOSH Recommendation for Environmental Exposure Limits. Such information is also shown in MSDSs and the HMIS referred to in paragraph 4.2. Carcinogenic substances are listed by OSHA in Category I for confirmed carcinogens, and in Category II for suspected carcinogens. Category I substances have standard exposure limits set at the lowest possible levels. Category II substances have standard exposure limits set to prevent acute or chronic effects.

4.3.4 Toxicity. Toxicity information for chemical compounds is available from various publications and from MSDSs.

4.3.4.1 EPA Toxic (T). Some chemical compounds have been designated by the EPA as toxic (T) in accordance with the criteria shown in Part 261, Subpart B, Section 261.11(a)(3) of 40CFR.* Some commercial chemical products are listed as toxic under Subpart D, Section 261.33(f).

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4.3.4.2 EPA Acute Hazardous Toxicity (H). Some chemical compounds have been designated by the EPA as acute hazardous (H) in toxicity in accordance with the criteria shown in Subpart B, Section 261.11(a)(2) of the above reference.* Some commercial chemical products are listed as acute hazardous in toxicity under Subpart D, Section 261.33(e).

4.3.4.3 Hazardous toxic constituents. A list of chemical compounds and substances, shown to have toxic effects on humans or other life forms, is contained in Appendix VIII to 40CFR Part 261 and the Registry of Toxic Effects of Chemical Substances.

4.4 Pollution and disposal.

4.4.1 Pollution potential. All items described in this standard should be assumed to have a pollution potential. However, to minimize this potential, the proper use, storage and disposal methods must be strictly followed.

4.4.2 Disposal of excess or unserviceable material. To minimize disposal problems, it is recommended that no more than a one year's supply of each item listed in this standard be stocked. When stocks have been declared excess or unserviceable, they will be disposed of in accordance with the Defense Utilization and Defense Disposal Manual, DOD 4160.21-M, and applicable DOD Policy Memoranda and the Consolidated HM/HW Disposal Guidance. Guidance can be obtained from your servicing Defense Property Disposal Office (DPDO) on procedures required for proper reporting and turn-in.

4.4.3 Disposal and storage of hazardous wastes. Items are classified and managed as hazardous wastes as defined by the Resource Conservation and Recovery Act (RCRA) of 1976 (Public Law 94-580). Items have been identified as meeting the characteristics (i.e., ignitable, corrosive, reactive or EP toxic) or are listed (i.e., toxic or acute hazardous) according to Identification and Listing of Hazardous Waste, Part 261; 40CFR; or have been determined to be hazardous wastes by declaration of the Defense Property Disposal Service (DPDS) in accordance with procedures set forth in DOD 4160.21-M. Disposal of such items must be managed in accordance with the Installation Environmental Office, the DPDO, or the Safety and Health Office to insure proper reporting of disposal and treatment actions to the US EPA and State; and must be managed in accordance with Federal, State and local laws. The three main disposal methods are turn-in to the DPDO, on-post disposal by installation personnel, or disposal by commercial contract. Hazardous wastes that cannot be used, or disposed of as stated in paragraph 4.4.3.2, must be stored under environmentally safe conditions until suitable methods of disposal are determined. Short-term storage (less than 90 days) requires proper containment (i.e., packaging and facilities) in accordance with section 262.34, Part 262 of the above reference. Long-term storage (greater than 90 days) requires permitting by the EPA or by the state under Public Law 94-580 of 1976 (RCRA), in compliance with the requirements of 40CFR Parts 264 and 265. Physical custody will be accomplished by the activity with conforming storage or most nearly conforming storage. When physical custody is in question, the Post Commander will make the final decision. In all cases where the wastes are to be collected, stored, transported

*Refers only to materials that have become waste materials.

and disposed of at a state or local permitted disposal facility, the identity and description of the waste must be maintained and recorded in accordance with Part 262 of the above reference. Transportation of the waste must be in accordance with Part 263 of the above reference, Standards Applicable to Transporters of Hazardous Waste.

4.4.3.1 Cleanup of liquid spills. To control the migration of spilled or leaking liquids, dike around the item with an inert, dry absorbent (e.g. clay, sawdust or vermiculite) or follow local spill plans. Control entry to the spill site and segregate salvageable materials away from the spill area. Initiate waste cleanup operations immediately in accordance with local procedures. The residue should be safely handled and transported to an approved or permitted disposal or storage facility. Packaging, labeling, transportation and record-keeping requirements for this waste material are determined by the appropriate Federal and State agencies and local procedures. It is recommended that all activities involving disposal preparation and transportation to commercial facilities be properly coordinated with the appropriate Federal and State agencies responsible for health and environmental aspects of hazardous materials. It is imperative that the proper description of waste accompany the packaged item at all times. Final disposal of the waste item should be accomplished by reutilization, transfer, donation or sales by DPDS in accordance with DOD 4160.21-M or by ultimate disposal as described in paragraph 4.4.3.2. Spill residue, including contaminants, to be turned in to the DPDO must first be properly identified, containerized, and labeled. For large scale spills that grossly contaminate the environment, the Chemical Transportation Emergency Center (CHEMTREC), can be called for assistance. Applicable procedures of the local spill control plan should be followed.

4.4.3.2 Ultimate disposal. Ultimate disposal shall be accomplished at a permitted or approved hazardous waste treatment or disposal facility designated by the Installation Environmental Office, DPDO, or Safety and Health Offices.

4.4.4 DISCLAIMER. RECOMMENDED DISPOSAL INSTRUCTIONS ARE FORMULATED FOR USE BY ELEMENTS OF THE DEPARTMENT OF DEFENSE. THE UNITED STATES OF AMERICA IN NO MANNER WHATSOEVER EITHER EXPLICITLY OR IMPLICITLY WARRANTS, STATES OR INTENDS SAID INSTRUCTION, TO HAVE ANY APPLICATION, USE OR VIABILITY BY OR TO ANY PERSON OR PERSONS CONTRACTING OUTSIDE THE DEPARTMENT OF DEFENSE OR ANY PERSON OR PERSONS CONTRACTING WITH ANY INSTRUMENTALITY OF THE UNITED STATES OF AMERICA AND DISCLAIMS ALL LIABILITY FOR SUCH USE. ANY PERSON USING THESE INSTRUCTIONS WHO IS NOT A MILITARY OR CIVILIAN EMPLOYEE OF THE UNITED STATES OF AMERICA SHOULD SEEK COMPETENT PROFESSIONAL ADVICE TO VERIFY AND ASSUME RESPONSIBILITY FOR THE SUITABILITY OF THESE INSTRUCTIONS TO THEIR PARTICULAR SITUATION REGARDLESS OF SIMILARITY TO A CORRESPONDING DEPARTMENT OF DEFENSE OR OTHER GOVERNMENT SITUATION.

5. DETAIL REQUIREMENTS

5.1 Acid-base indicators. Acid-base indicators are highly colored organic dye molecules possessing acidic or basic functional groups. In solution, variations in pH cause the indicator molecule to undergo a color change because of structural rearrangement. The color changes in a pH interval of about 2 units. The amount of indicator used in a titration is kept minimal to prevent a contribution to the pH, so that only a

small amount of titrant is required for the color change. Acid-base indicators are commercially available covering the pH scale from 0.0 to 14.0 in aqueous solutions. For nonaqueous titrations, the pH of color change is different than in water, and the selection or choice of indicators is empirical. Table I lists some commercially available normal acid-base indicators, covering the pH range from 0.0 to 14.0, and their color changes. The indicators are listed in consecutive order by pH range.

TABLE I
NORMAL ACID-BASE INDICATORS

COMMON NAME	CHEMICAL NAME	APPROXIMATE pH RANGE	COLOR CHANGE
Methyl Violet	----	0.0 to 1.6	Yellow to Blue
Crystal Violet, ACS	Hexamethylpararosaniline Chloride	0.0 to 1.8	Yellow to Blue
Ethyl Violet	----	0.0 to 2.4	Yellow to Blue
Malachite Green	[4-[p-(Dimethylamino)-α-phenylbenzylidene]-2,5-cyclohexadien-1-ylidene]-dimethylammonium Chloride	0.0 to 2.0	Yellow to Bluegreen
Brilliant Green	----	0.0 to 2.6	Yellow to Green
Malachite Green	(Oxalate form)	0.2 to 1.8	Yellow to Bluegreen
Methyl Green	Heptamethyl-p-rosaniline Chloride	0.2 to 1.8	Yellow to Blue
Picric Acid, ACS	2,4,6-Trinitrophenol	0.2 to 1.0	Colorless to Yellow
*Cresol Red	o-Cresolsulfonphthalein (Free acid and sodium salt forms)	1.0 to 2.0	Red to Yellow
Quinaldine Red	2-(p-Dimethylaminostyryl)quinoline Ethiodide	1.0 to 2.0	Colorless to Red
Para Methyl Red	p-(p-Dimethylaminophenylazo)benzoic Acid, Sodium Salt	1.0 to 3.0	Red to Yellow
Basic Fuchsin	2-Methyl-4,4'-[(4-imino-2,5-cyclohexadien-1-ylidene)-methylene]dianiline Monohydrochloride	1.0 to 3.1	Purple to Red
Metanil Yellow	4-(3-Sulfobenzeneazo)diphenylamine, Sodium Salt	1.2 to 2.4	Red to Yellow
*Thymol Blue, ACS	Thymolsulfonphthalein (Free acid and sodium salt forms)	1.2 to 2.8	Red to Yellow

TABLE I. Continued

COMMON NAME	CHEMICAL NAME	APPROXIMATE pH RANGE	COLOR CHANGE
*m-Cresol Purple	m-Cresolsulfonphthalein (Free acid and sodium salt forms)	1.2 to 2.8	Red to Yellow
Orange IV	p-[(p-Anilinophenyl)azo]-benzenesulfonic Acid, Sodium Salt	1.4 to 2.8	Red to Yellow
Aminoazotoluene	4-(o-Tolylazo)-o-toluidine	1.4 to 2.8	Orange to Yellow
Quinaldine Red	5-Dimethylamino-2-styrylethyl-quinolinium Iodide	1.4 to 3.2	Colorless to Red
Methyl Violet 2B	----	1.5 to 3.2	Blue to Violet
----	p-Phenylazoaniline	1.8 to 3.3	Orange to Yellow
Erythrosin B	Erythrosine, Disodium Salt	2.2 to 3.4	Orange to Red
Phloxine B (Acid Red 92)	2',4',5',7'-Tetrabromo-3,4,5,6-tetrachloro-fluorescein, Sodium Derivative, Sodium Salt	2.1 to 3.3	Colorless to Pink
Benzopurpurin 4B	----	2.2 to 4.2	Violet to Red
----	N,N-Dimethyl-p-(m-tolylazo)aniline	2.6 to 4.8	Red to Yellow
----	2,4-Dinitrophenol (15% H_2O added)	2.6 to 4.0	Colorless to Yellow
----	3',3",5',5"-Tetrabromophenolphthalein Ethyl Ester, Potassium Salt	3.0 to 4.2	Yellow to Blue
Methyl Yellow	p-Dimethylaminoazobenzene or N,N-Dimethyl-p-phenylazoaniline	2.8 to 4.4	Red to Yellow
*Bromophenol Blue, ACS	3',3",5',5"-Tetrabromophenolsulfonphthalein (Free acid and sodium salt forms)	3.0 to 4.6	Yellow to Blue

TABLE I. Continued

COMMON NAME	CHEMICAL NAME	APPROXIMATE pH RANGE	COLOR CHANGE
Congo Red	Sodium Diphenyldiazo-bis-α-naphthylamine Sulfonate	3.0 to 5.0	Blue to Red
----	3-Nitrosalicylaldhyde	3.0 to 5.0	Colorless to Yellow
Methyl Orange-Xylene Cyanole Solution	----	3.2 to 4.2	Purple to Green
Methyl Orange, ACS	4-[p-(Dimethylamino)phenylazo]benzenesulfonic Acid, Sodium Salt	3.2 to 4.4	Pink or Red to Yellow
Bromochlorophenol Blue	3',3"-Dibromo-5',5"-dichlorophenolsulfon-phthalein, Sodium Salt	3.2 to 4.8	Yellow to Blue
Ethyl Orange	4-(p-Diethylaminophenylazo)benzenesulfonic Acid, Sodium Salt	3.4 to 4.8	Red to Yellow
----	3-(4-Dimethylamino-1-naphthylazo)-4-methoxy-benzenesulfonic Acid	3.4 to 4.8	Violet to Yellow
*Bromocresol Green, ACS	3',3",5',5"-Tetrabromo-m-cresolsulfonphthalein (Free acid and sodium salt forms)	3.8 to 5.4	Yellow to Blue
Resazurin	7-Hydroxy-3H-phenoxazin-3-one-10-oxide, Sodium Salt	3.8 to 6.4	Orange to Violet
Gallein	Pyrogallolphthalein	3.8 to 6.6	Light Brown to Yellow Rose
α-Naphthyl Red	4-Phenylazo-1-naphthylamine Hydrochloride	4.0 to 5.6	Red to Yellow
Ethyl Red	Quinolinium, 1-ethyl-2-[(1-ethyl-4(1H)-quinolinylidine)methyl]-, Iodide	4.0 to 5.8	Colorless to Red
Chrysoidine Orange	2,4-Diaminoazobenzene Hydrochloride	4.0 to 7.0	Orange to Yellow
Methyl Red, ACS	(I) o-[[p-(Dimethylamino)phenyl]azo]benzoic Acid (II) Sodium salt form, (III) Hydrochloride form	4.2 to 6.2	Pink to Yellow

TABLE I. Continued

COMMON NAME	CHEMICAL NAME	APPROXIMATE pH RANGE	COLOR CHANGE
----	4-(p-Ethoxyphenylazo)-m-phenylenediamine Monohydrochloride	4.4 to 5.8	Orange to Yellow
Alizarin Red S	3-Alizarinsulfonic Acid, Sodium Salt	4.6 to 6.0	Yellow to Red
Propyl Red	2-(p-Dipropylaminophenylazo)benzoic Acid	4.8 to 6.6	Red to Yellow
----	o-Nitrophenol	5.0 to 6.2	Colorless to Yellow
Eriochrome Black T	1-(1-Hydroxy-2-naphthylazo)-5-nitro-2-naphthol-4-sulfonic Acid, Sodium Salt	5.0 to 6.5	Red to Blue
*Bromocresol Purple	5',5"-Dibromo-o-cresolsulfonphthalein (Acid and sodium salt forms)	5.2 to 6.8	Yellow to Purple
Chlorophenol Red	3',3"-Dichlorophenolsulfonphthalein	5.2 to 6.8	Yellow to Red
----	*p-Nitrophenol (Acid and sodium salt forms)	5.4 to 6.6	Colorless to Yellow
Alizarin	1,2-Dihydroxyanthraquinone	5.6 to 7.2	Yellow to Red
Nitrazine Yellow	2-(2,4-Dinitrophenylazo)-1-naphthol-3,6-disulfonic Acid, Sodium Salt	6.0 to 7.0	Yellow to Blue
*Bromothymol Blue, ACS	3',3"-Dibromothymolsulfonphthalein (Acid and sodium salt forms)	6.0 to 7.6	Yellow to Blue
Rosolic Acid	4-[Bis-(p-hydroxyphenyl)methylene]-2,5-cyclohexadien-1-one	6.0 to 8.0	Yellow to Red
Brilliant Yellow	----	6.6 to 8.0	Yellow to Orange
----	3,4,5,6-Tetrabromophenolsulfonphthalein	6.6 to 8.2	Yellow to Purple
*Phenol Red, ACS	Phenolsulfonphthalein (Acid and sodium salt forms)	6.8 to 8.2	Yellow to Red

TABLE I. Continued

COMMON NAME	CHEMICAL NAME	APPROXIMATE pH RANGE	COLOR CHANGE
Neutral Red	3-Amino-7-dimethylamino-2-methylphenazine Chloride	6.8 to 8.0	Red to Amber
----	m-Nitrophenol	6.8 to 8.6	Colorless to Yellow
*Cresol Red	o-Cresolsulfonphthalein (Acid and sodium salt forms)	7.0 to 8.8	Yellow to Red
Curcumin	1,7-Bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione	7.4 to 8.6	Yellow to Red
*m-Cresol Purple	m-Cresolsulfonphthalein (Acid and sodium salt forms)	7.4 to 9.0	Yellow to Purple
----	4,4'-Bis(4-amino-1-naphthylazo)-2,2'stilbenedisulfonic Acid	8.0 to 9.0	Blue to Red
*Thymol Blue, ACS	Thymolsulfonphthalein (Acid and sodium salt forms)	8.0 to 9.2	Yellow to Blue
----	o-Cresolphthalein	8.2 to 9.8	Colorless to Red
----	p-Naphtholbenzein	8.2 to 10.0	Orange to Blue
*Phenolphthalein, ACS	3,3-Bis(p-hydroxyphenyl)phthalide (Acid and sodium salt forms)	8.0 to 8.2 8.2 to 8.6 8.6 to 10.0	Colorless to Pale Pink Pale Pink to Pink Pink to Red
----	Ethyl bis(2,4-dinitrophenyl)acetate	8.4 to 9.6	Colorless to Blue
Thymolphthalein, ACS	2',2"-Dimethyl-5',5"-diisopropylphenolphthalein	9.3 to 10.5	Colorless to Blue
Nile Blue A	5-Amino-9-(diethylamino)benzo[α]-phenazoxonium Chloride	9.4 to 10.6	Blue to Red
Alizarin Yellow R	5-(p-Nitrophenylazo)-salicylic Acid, Sodium Salt	10.0 to 12.0	Yellow to Red

TABLE I. Continued

COMMON NAME	CHEMICAL NAME	APPROXIMATE pH RANGE	COLOR CHANGE
Aniline Blue (Acid Blue 22)	----	10.0 to 13.0	Blue to Orange
Curcumin	1,7-Bis(4-hydroxy-3-methoxyphenyl)-1,6-hepta-diene-3,5-dione	10.2 to 11.8	Red to Orange
Malachite Green	(Hydrochloride form)	10.5 to 12.5	Blue to Colorless
Alizarin	1,2-Dihydroxyanthraquinone	11.0 to 12.4	Red to Purple
Azo Violet	p-Nitrobenzeneazoresorcinol	11.0 to 13.0	Yellow to Violet
Tropaeolin O (Resorcinol Yellow)	p-(2,4-Dihydroxyphenylazobenzenesulfonic Acid, Sodium Salt	11.1 to 12.7	Yellow to Orange Brown
*Indigo Carmine	5,5'-Indigodisulfonic Acid, Disodium Salt	11.4 to 13.0	Blue to Yellow
----	2,4,6-Trinitrotoluene	11.5 to 13.0	Colorless to Orange
Orange G (Acid Orange 10)	----	11.5 to 14.0	Yellow to Pink
Basic Fuchsin	2-Methyl-4,4'-[(4-imino-2,5-cyclohexadien-1-ylidene)methylene]dianiline Monohydrochloride	11.6 to 14.0	Red to Colorless
Acid Fuchsin	Rosaniline Trisulfonic Acid, Disodium Salt	12.0 to 14.0	Red to Colorless
Clayton Yellow (Thiazol Yellow G)	----	12.0 to 14.0	Yellow to Red

* Sodium salt form directly soluble in water.

5.1.1 Specifications for acid-base indicators.

5.1.1.1 Chemicals, Analytical; General Specification For - Federal Specification O-C-265. This specification covers analytical reagent grade chemicals conforming to the requirements for ACS grade reagents and USP reagents, indicators and solutions. The following ACS and USP reagent acid-base indicators are covered by this specification.

Azo Violet (USP)
Brilliant Green (USP)
Bromocresol Green (ACS)
Bromocresol Purple (USP)
Bromophenol Blue (ACS)
Bromothymol Blue (ACS)
Congo Red (USP)
Cresol Red (USP)
Crystal Violet (ACS)
Malachite Green Oxalate (USP)
Methyl Orange (ACS)
Methyl Red (ACS)
Methyl Yellow (USP)
p-Naphtholbenzein (USP)
Neutral Red (USP)
Nile Blue Hydrochloride (USP)
Phenolphthalein (ACS)
Phenol Red (ACS)
Picric Acid (ACS)
Quinaldine Red (USP)
Sodium Alizarinsulfonate (USP)
Thymol Blue (ACS)
Thymolphthalein (ACS)

5.1.1.2 Bromophenol Blue Solution; Indicator, 3.0 to 4.6 pH Range - MIL-B-11722.

5.1.1.2.1 Technical description. This specification describes bromophenol blue indicator solution for indicating a pH change in the range from less than 3.0 to 4.6 of initially colorless aqueous solutions. The indicator solution shall contain 0.4 gram of bromophenol blue (tetrabromophenolsulfonphthalein) per liter of distilled water. The pH of the solution shall be adjusted to be between 3.5 and 4.1 by use of reagent grade hydrochloric acid or sodium hydroxide. When tested by means of buffer solutions at pHs of 3.0, 3.8 and 4.6, four drops of the indicator solution in 10 mL of each buffer solution shall be colored yellow, yellow-green, and blue, respectively.

5.1.1.2.2 Use. The bromophenol blue indicator solution is intended for use in the determination of the pH of water during the water purification process.

5.1.1.3 Bromothymol Blue Solution; Indicator, 6.0 to 7.6 pH Range - MIL-B-11845.

5.1.1.3.1 Technical description. This specification describes bromothymol blue indicator solution for indicating a pH change from less than 6.0 to 7.6 of initially colorless aqueous solutions. The indicator solution shall contain 0.4 gram of bromothymol blue (dibromothymolsulfonphthalein) per liter of a 50% water and 50% methanol by volume solution. The pH of the solution shall be adjusted to be between 6.5 and 7.1 by use of reagent grade hydrochloric acid or sodium hydroxide. When tested by means of buffer solutions at pHs of 6.0, 6.8, and 7.6, four drops of the indicator solution in 10 mL of each buffer solution shall be colored yellow, green, and blue, respectively.

5.1.1.3.2 Use. The bromothymol blue indicator solution is intended for use in the determination of the pH of water during the water purification process.

5.1.1.4 Indicator Solutions, pH Determination (For Water Supply Testing) - MIL-I-536.

5.1.1.4.1 Technical description. This specification describes two types of indicator solutions suitable for use in the determination of pH values of clear waters by colorimetric comparison with colored disk standards. These indicator solutions are not commercially standard.

a. Type I - The indicator solution shall be a mixture of 90% distilled water and 10% methanol by volume, containing 0.140 ± 0.005 g/L of bromocresol purple (dibromo-o-cresolphthalein) and 0.210 ± 0.005 g/L bromocresol green (tetrabromo-m-cresolsulfonphthalein). The pH of the solution shall be adjusted to be between 4.9 and 5.5 by use of reagent grade hydrochloric acid or sodium hydroxide. This indicator solution shall be suitable for use in the determination of pH values of water having a pH range from 4.4 to 6.0.

b. Type II - The indicator solution shall be a mixture of 90% distilled water and 10% methanol by volume, containing 0.0920 ± 0.0005 g/L cresol red (o-cresolsulfonphthalein) and 0.1230 ± 0.005 g/L thymol blue (thymolsulfonphthalein). The pH of the solution shall be adjusted to be between 8.1 and 8.7 by use of reagent grade hydrochloric acid or sodium hydroxide. This indicator solution shall be suitable for use in the determination of pH values of water having a pH range from 7.6 to 9.2.

5.1.1.4.2 Use.

a. Type I indicator solution is intended for use in the determination of pH values of water having a pH range from 4.4 to 6.0.

b. Type II indicator solution is intended for use in the determination of pH values of water having a pH range from 7.6 to 9.2.

5.1.1.5 Indicator Solution, pH Determination - MIL-I-52701.

5.1.1.5.1 Technical description. This specification describes an indicator solution that shall produce a color for specific pH values of

water that visually match color standards of a master color disk, conforming to MIL-D-537, Type I, Class B, when tested as specified with buffer solutions of pH 3.0 to 11.0 inclusive in increments of 1 pH. The composition of the indicator solution is not specified.

5.1.1.5.2 Use. The indicator solution is intended for use in determining the pH of water from 3.0 to 11.0 in increments of 1 pH.

5.1.1.6 Metanil Yellow, Reagent - MIL-M-50075.

5.1.1.6.1 Technical description. This specification describes a reagent grade of metanil yellow (sodium salt of 4-(3-sulfobenzeneazo) diphenylamine) for use as a pH indicator. The indicator shall change to a red color at a pH of 1.2 ± 0.2 and shall change to a yellow color at a pH of 2.3 ± 0.2 when tested as an indicator solution of 0.01 g in 10 mL of 95% ethanol.

5.1.1.6.2 Use. Metanil yellow (tropaeolin G) is intended for use as an acid-base indicator solution at a concentration of 0.1% in ethyl alcohol for the pH change of approximately 1.2 to 2.4 with a color change of red to yellow.

5.1.1.7 Water-Testing Chemicals, Boiler, Shipboard Use - MIL-W-15000.

5.1.1.7.1 Technical description. This specification describes boiler-water testing chemicals including Class D - phenolphthalein, ACS, reagent, powder, and Class E - methyl purple indicator which is composed of a dry mixture of 0.055 ± 0.009 gram of Acid Blue 5 dye and 0.045 ± 0.007 gram of methyl red, sodium salt, contained in a gelatin capsule. The performance of the indicator shall be tested as specified by titration of a sodium carbonate solution with nitric acid, with the color of the indicator changing at the end-point from green to purple at a pH of 4.9 ± 0.3. Methyl purple indicator functions in the pH range of 5.4 to 5.1 to 4.8, with color changes from green to gray to purple. For use as an alkalinity test indicator, an indicator solution is prepared by dissolving the contents of a capsule in 100 mL of double-distilled water.

5.1.1.7.2 Use. Methyl purple indicator is intended for military use on shipboard for the chemical testing and control of boiler feedwater.

5.2 Fluorescent acid-base indicators. Fluorescent acid-base indicators fluoresce under the influence of ultraviolet light and their fluorescence is highly dependent on the pH of the solution. No change in indicator solution concentration is usually required when fluorescent acid-base indicators are employed for the titration of strongly colored or turbid solutions. Table II lists some commercially available fluorescent acid-base indicators covering the pH scale from 0.0 to 14.0. The indicators are listed in consecutive order by pH range.

TABLE II
FLUORESCENT ACID-BASE INDICATORS

COMMON NAME	CHEMICAL NAME	pH RANGE
Coumarin 4	7-Hydroxy-4-methyl Coumarin	0.0 to 2.0
Eosin Y (Yellowish)	2',4',5',7'-Tetrabromofluorescein, Disodium Salt (Also free acid form)	0.0 to 3.0
Anthranilic Acid	o-Aminobenzoic Acid	1.5 to 3.0
----	7-Amino-1,3-naphthalenedisulfonic Acid, Monosodium Salt	2.0 to 4.0
----	1-Naphthoic Acid	2.5 to 3.5
Salicylic Acid, ACS	o-Hydroxybenzoic Acid	2.5 to 4.0
Erythrosin B (Bluish)	----	2.5 to 4.0
Phloxine B (Acid Red 92)	2',4',5',7'-Tetrabromo-3,4,5,6-tetrachlorofluorescein, Sodium Derivative, Sodium Salt	2.5 to 4.0
----	4-Amino-1-naphthalenesulfonic Acid	3.0 to 4.0
----	3-Hydroxy-2-naphthoic Acid	3.0 to 6.8
Morin	2',3,4',5,7-Pentahydroxyflavone	3.1 to 4.4
----	o-Phenylenediamine	3.1 to 4.4
----	p-Phenylenediamine	3.1 to 4.4
----	o-Anisaldehyde	3.1 to 4.4
Fluorescein, And Disodium Salt	----	3.8 to 5.0
Chromotropic Acid Disodium Salt, ACS	4,5-Dihydroxy-2,7-naphthalenedisulfonic Acid, Disodium Salt	4.0 to 6.0
----	2',7'-Dichlorofluorescein	4.0 to 6.0

TABLE II. Continued

COMMON NAME	CHEMICAL NAME	pH RANGE
Resorufin	----	4.4 to 6.4
Anthranilic Acid	o-Aminobenzoic Acid	4.5 to 6.0
Acridine	----	5.2 to 6.6
Lacmoid (Resorcin Blue)	----	5.8 to 7.0
----	5-Amino-2,3-dihydro-1,4-phthalazinedione	6.0 to 7.0
Quinoline	----	6.2 to 7.2
Coumarin 4	7-Hydroxy-4-methyl Coumarin	6.5 to 8.0
β-Naphthol	2-Naphthol	6.5 to 8.5
----	2-Naphthol-6,8-disulfonic Acid, Dipotassium Salt	7.0 to 8.5
α-Naphthol	1-Naphthol	7.0 to 9.0
----	1-Naphthol-3,6-Disulfonic Acid, Disodium Salt	7.0 to 9.0
----	2-Naphthol-3,6-Disulfonic Acid, Disodium Salt	7.0 to 9.0
----	1-Naphthol-4-sulfonic Acid, Sodium Salt	8.0 to 9.0
----	1-Naphthol-2-sulfonic Acid, Potassium Salt	8.0 to 9.0
Coumarin	----	8.0 to 9.5
Morin	2',3,4',5,7-Pentahydroxyflavone	8.0 to 9.8
Acridine Orange	3,6-Bis(dimethylamino)acridine Hydrochloride	8.0 to 10.4
----	2-(o-Hydroxyphenyl)benzothiazole	9.3
----	4-Amino-1-naphthalenesulfonic Acid	10.0 to 12.0

TABLE II. Continued

COMMON NAME	CHEMICAL NAME	pH RANGE
----	7-Amino-1,3-naphthalenedisulfonic Acid, Monosodium Salt	12.0 to 13.0
----	4-Amino-1-naphthalenesulfonic Acid	12.0 to 14.0
Anthranilic Acid	o-Aminobenzoic Acid	12.5 to 14.0

5.2.1 Specification for fluorescent acid-base indicators.

5.2.1.1 Fluorescein Sodium, Reagent - MIL-F-11368.

5.2.1.1.1 Technical description. This specification describes disodium fluorescein with a minimum purity of 98.0% by weight (anhydrous basis), and a maximum loss on drying at 115° to 120°C of 7.0% by weight. A solution of the reagent shall pass a sensitivity test for indicator colors by production of a distinct pink color and a bright yellow-green fluorescent color when tested as specified, with the yellow-green color appearing in an alkaline solution.

5.2.1.1.2 Use. Fluorescein sodium is intended for use as a fluorescent acid-base indicator in the pH range of 3.8 to 5.0. Fluorescein sodium is also intended for use as an adsorption indicator.

5.3 Adsorption indicators. Adsorption indicators are organic compounds (dyes) that are adsorbed by colloidal precipitates more strongly on one side of the equivalence point than on the other in precipitation titrations. An indicator reaction takes place on the surface of the precipitate, and in certain cases the dye undergoes an abrupt color change in the process of being adsorbed. The pH of the solution must be such to assure that the ionic form of the indicator predominates. Most adsorption indicators are weak acids, and their use is confined to neutral or slightly acidic solutions where the indicator exists predominantly as an anion. Few cationic indicators are known that are suitable for titrations in strongly acidic solutions. Table III lists some commercially available adsorption indicators for the titration of a variety of ionic species.

TABLE III
ADSORPTION INDICATORS

COMMON NAME	CHEMICAL NAME	FOR IONIC SPECIES
Alizarin	1,2-Dihydroxyanthraquinone	Nitrate.
Alizarin Red S	3-Alizarinsulfonic Acid, Sodium Salt	Ferrocyanide; fluoride; molybdate; thiocyanate; sulfate.
Biebrich Scarlet	----	Bromide; chloride.
Bromocresol Purple	5',5"-Dibromo-o-cresolsulfonphthalein (Acid and sodium salt forms)	Bromide; chloride.
Bromophenol Blue	3',3",5',5"-Tetrabromophenolsulfonphthalein (Acid and sodium salt forms)	Bromide; chloride; iodide; thiocyanate; silver; thallium; mercury (with chloride).
Congo Red	Sodium Diphenylazo-bis-α-naphthylamine Sulfonate	Bromide; chloride; iodide.
----	2'7'-Dichlorofluorescein	Bromide; chloride.
----	4',5'-Dichlorofluorescein	Borate; bromide; chloride; iodide.
----	1,5-Diphenylcarbohydrazide	Bromide; chloride; cyanide; iodide; thiocyanate.
Eosin (Yellowish) (Free acid form) Eosin Y (Disodium Salt)	2',4',5',7'-Tetrabromofluorescein	Bromide; iodide; permanganate; sulfate; thiocyanate.
Fluorescein, Sodium Derivative, Sodium Salt	----	Bromide; chloride; cyanide; iodide; oxalate; sulfate; thiocyanate.
Methyl Red	2-[p-(Dimethylaminophenylazo]benzoic Acid	Zinc (with ferrocyanide).
Methyl Violet	----	Silver (with chloride).

TABLE III. Continued

COMMON NAME	CHEMICAL NAME	FOR IONIC SPECIES
Orthochrome T	----	Lead (II) (with chromate).
Rhodamine 6G	----	Bromide; chloride; silver (with bromide).
Rose Bengal	4,5,6,7-Tetrachloro-2',4',5',7'-tetraiodofluorescein, Sodium Derivative, Sodium Salt	Iodide.
Tartrazine	----	Silver (with halides).
Thorin	o-(3,6-Disulfo-2-hydroxy-1-naphthylazo)benzenearsonic Acid, Disodium Salt	Sulfate (with barium).

5.3.1 Specification for adsorption indicators.

5.3.1.1 Fluorescein Sodium, Reagent - MIL-F-11368.

5.3.1.1.1 Technical description. Refer to paragraph 5.2.1.1.1.

5.3.1.1.2 Use. Fluorescein sodium is intended for use as an adsorption indicator for the ionic species bromide, chloride, cyanide, iodide, oxalate, sulfate and thiocyanate by titration with appropriate metal ion solutions.

5.4 Metallochromic indicators. Metallochromic indicators are organic chelating agents, containing a chromophoric (color-forming) group, that forms stable brightly colored complexes with most metal ions. These indicators are useful in complexometric titrations which are methods based on complex formation with metals. Complexometric titrations are performed mainly with solutions of aminopolycarboxylic acids, which are chelating agents, with the most popular being ethylenediaminetetraacetic acid (EDTA). Complexometric titrations with chelating agents are called chelometric titrations. The indicator is usually a highly colored dye that forms a complex of a different color with the metal being titrated. These indicators have different colors in their metallized and free forms, and can serve as end-point detectors in EDTA titrations. The metal-indicator complex should be 10 to 100 times less stable than the metal chelate complex. It is necessary that the rate at which the metal-indicator complex reacts with EDTA be rapid, so the end-point will not be overrun. Table IV lists some commercially available metallochromic indicators for the titration of a variety of metal cations. Metallochromic indicators can also be used for the titration of anions that form nonionized compounds with metal cations. The end-point is indicated by a color change caused by the first slight excess of metal cation.

TABLE IV
METALLOCHROMIC INDICATORS

COMMON NAME	CHEMICAL NAME	FOR METAL CATIONS
Alizarin Fluorine Blue	----	Ba(II), Ca(II), Cd(II), Co(II), Cu(II), In(III), Pb(II), Sr(II).
Alizarin Red S	3-Alizarinsulfonic Acid, Sodium Salt	Sc(III), Th(IV), Rare Earths (III).
----	5-Amino-2,3-dihydro-1,4-phthalizinedione	Cu(II).
Arsenazo I	o-(1,8-Dihydroxy-3,6-disulfo-2-naphthylazo)benzenearsonic Acid, Trisodium Salt	Ca(II), Cu(II), Fe(III), Mg(II), Th(IV).
Arsenazo III	o-(1,8-Dihydroxy-3,6-disulfonaphthylene-2,7-bisazo)bisbenzenearsonic Acid	Ca(II), Cd(II), Th(IV), V(IV), Zn(II), Zr(IV).
----	Aurintricarboxylic Acid, Triammonium Salt	Al(III), Ca(II), Fe(III), Mg(II).
Calcein (Fluorexon)	Bis[N,N-bis-(carboxymethylamino)aminomethyl]fluorescein	Ba(II), Ca(II), Cu(II), Mn(II), Sr(II).
Calcon	----	Ca(II), Cd(II), Mg(II), Mn(II), Zn(II).
Calmagite	3-Hydroxy-4-(2-hydroxy-4-sulfo-1-naphthylazo)-2-naphthalene Carboxylic Acid	Mg(II).
Carminic Acid	----	Th(IV), Zr(IV), Rare Earths (III).
Chromotrope 2R	----	Th(IV).
o-Cresolphthalein Complexon®	o-Cresolphthalexon (Free acid form)	Ba(II), Ca(II), Cd(II), Mg(II), Sr(II).
p-Dimethylaminobenzalrhodanine	5-[p-(Dimethylamino)benzylidene]rhodanine	Ag(I).
----	sym-Diphenylcarbazone, ACS	Cd(II), Ga(III), Hg(II), Mn(II), Ni(II), Pb(II), V(IV).
----	1,5-Diphenylcarbohydrazide, ACS	Hg(II), V(IV).

TABLE IV. Continued

COMMON NAME	CHEMICAL NAME	FOR METAL CATIONS
Dithizone, ACS	Diphenylthiocarbazone	Bi(II), Ca(II), Cd(II), Fe(III), In(III), Mg(II), Mn(II), Ni(II), Pb(II), Th(IV), V(IV), Zn(II), Rare Earths (III).
Eriochrome Black T	1-(1-Hydroxy-2-naphthylazo)-5-nitro-2-naphthol-4-sulfonic Acid, Sodium Salt	Ba(II), Cd(II), In(III), Mg(II), Mn(II), Pb(II), Sc(III), Sr(II), Zn(II), Zr(IV), Rare Earths (III).
Eriochrome Cyanine R	----	Ba(II), Ca(II), Co(II), Cu(II), Fe(III).
Hematoxylin	----	Al(III), Bi(II), Th(IV), Zr(IV).
----	3-Hydroxy-2-naphthoic Acid	Al(III), Fe(III).
Hydroxy Naphthol Blue, ACS	1-(2-Naphtholazo-3,6-disulfonic Acid)-2-naphthol-4-sulfonic Acid	Ca(II).
----	8-Hydroxy-4-nitroso-2,7-naphthalenedisulfonic Acid, Disodium Salt	Cu(II), Ni(II).
----	8-Hydroxy-5-quinolinesulfonic Acid	Cd(II), Zn(II).
----	o-[2-[α-(2-Hydroxy-5-sulfophenylazo)benzilidene]hydrazino]benzoic Acid, Sodium Salt	Al(III), Cd(II), Ce(III), Cr(III), Co(II), In(III), Fe(III), Sc(III), Zn(II), Ni(II), Pb(II), Mn(II), Rare Earths (III).
Metalphthalein	----	Ba(II), Ca(II), Cd(II), Mg(II), Sr(II).
----	N-(p-Methoxyphenyl)-p-phenylenediamine Hydrochloride	Al(III), Cd(II), Cu(II), Fe(III), Pb(II), Zn(II).
Methyl Calcein	2',7-Bis[[(carboxymethyl)methylamino]methyl]fluorescein	Ba(II), Ca(II), Cd(II), Mg(II), Sr(II).

TABLE IV. Continued

COMMON NAME	CHEMICAL NAME	FOR METAL CATIONS
Methylene Blue	3,7-Bis(dimethylamino)phenazathionium-chloride	Cd(II), Co(II), Cu(II), Ni(II), Zn(II).
Methylthymol Blue	3,3'-Bis[N,N-di(carboxymethyl)aminomethyl]-thymolsulfonphthalein, Sodium Salt	Ba(II), Bi(II), Ca(II), Cd(II), Co(II), Cu(II), Fe(III), Hg(II), In(III), Mg(II), Mn(II), Pb(II), Sc(II), Sn(II), Sr(II), Th(IV), Zn(II), Zr(IV), Rare Earths (III).
Morin	2',3,4',5,7-Pentahydroxyflavone	Ga(III), In(III).
Murexide	Acid Ammonium Purpurate	Ca(II), Co(II), Cu(II), Mn(II), Ni(II), Sc(III), Zn(II).
PAN	1-(2-Pyridylazo)-2-naphthol	Al(III), Bi(II), Ca(II), Cd(II), Co(II), Cu(II), Fe(III), Ga(III), Hg(II), In(III), Mg(II), Mn(II), Ni(II), Pb(II), Sc(III), Th(IV), Tl(III), V(IV), Zn(II).
PAR	4-(2-Pyridylazo)resorcinol, Monosodium Salt	Al(III), Ba(II), Bi(II), Cd(II), Cu(II), Ga(III), Hg(II), In(III), Mn(II), Ni(II), Pb(II), Sr(II), Tl(III), Zn(II), Rare Earths (III).
Pyrocatechol Violet	Pyrocatecholsulfonphthalein	Bi(II), Cd(II), Co(II), Cu(II), Fe(III), Ga(III), In(III), Mg(II), Mn(II), Ni(II), Pb(II), Th(IV), Zn(II), Rare Earths (III).
Pyrogallol Red	Pyrogallolsulfonphthalein	Bi(II), Co(II), Ni(II), Pb(II).
----	8-Quinolinol, ACS	Cd(II), Cu(II), Mn(II), Ni(II), Pb(II), Zn(II).
Rhodizonic Acid, Disodium Derivative and Dipotassium Derivative	----	Ba(II), Rare Earths (III).

TABLE IV. Continued

COMMON NAME	CHEMICAL NAME	FOR METAL CATIONS
Salicylic Acid, ACS	o-Hydroxybenzoic Acid	Fe(III).
SNAZOXS	8-Hydroxy-7-[(4-sulfo-1-naphthyl)azo]-5-quinolinesulfonic Acid	Bi(II), Cd(II), Co(II), Cu(II), Fe(III), Hg(II), In(III).
SPADNS	4,5-Dihydroxy-3-[(p-sulfonphenyl)azo]-2,7-naphthalene Disulfonic Acid, Trisodium Salt	Ni(II), Pb(II), Zn(II), Rare Earths (III).
Sulfosalicylic Acid, ACS	5-Sulfosalicylic Acid	Fe(III), Th(IV), Zr(IV).
----	1-(2-Thiazolylazo)-2-naphthol	Co(II), Cu(II), Pb(II), Ni(II), Zn(II).
Thionine	3,7-Diaminophenothiazonium Chloride	Al(III), Fe(III), Hg(II), Pb(II).
Thorin	o-(3,6-Disulfo-2-hydroxy-1-naphthylazo)-benzenearsonic Acid, Disodium Salt	Th(IV), V(IV).
Tiron	4,5-Dihydroxy-m-benzenedisulfonic Acid, Disodium Salt	Fe(III), Mn(II), Mo(IV), Ti(IV).
Variamine Blue B Hydrochloride	N-(p-Methoxyphenyl)-p-phenylenediamine Monohydrochloride	Cd(II), Cu(II), Fe(III), Pb(II), Zn(II).
Xylenol Orange	----	Bi(II), Cd(II), Ca(II), Cu(II), Fe(III), Hg(II), In(III), Pb(II), Sc(III), Th(IV), Tl(III), V(IV), Zn(II), Zr(IV).
Zincon	----	Ca(II), Hg(II), Zn(II).

5.4.1 Specifications for metallochromic indicators.

5.4.1.1 Chemicals, Analytical; General Specification For - Federal Specification O-C-265. The following ACS and USP reagent metallochromic indicators are covered by this specification:

Aurintricarboxylic Acid Ammonium Salt (ACS)
s-Diphenylcarbazone (ACS)
1,5-Diphenylcarbohydrazide (ACS)
Dithizone (ACS)
Eriochrome Black T (USP)
Hydroxy Naphthol Blue (ACS)
8-Quinolinol (ACS)
Salicylic Acid (ACS)
Xylenol Orange (USP)

5.4.1.2 p-Dimethylaminobenzalrhodanine, Reagent - MIL-D-11318.

5.4.1.2.1 Technical description. This specification describes p-dimethylaminobenzalrhodanine (5-(p-dimethylaminobenzylidene)rhodanine) with the following chemical characteristics:

a. Solubility in acetone: 0.20 g in 100 mL of acetone to give a clear solution.

b. Residue on ignition: 0.20% by weight maximum.

c. Sensitivity: An alcoholic solution of the indicator shall produce a distinct reddish color with a solution of silver nitrate when tested as specified.

5.4.1.2.2 Use. p-Dimethylaminobenzalrhodanine is intended for use as an indicator for the detection of silver, mercury, copper, gold, platinum and palladium ions.

5.4.1.3 Water-Testing Chemicals, Boiler, Shipboard Use - MIL-W-15000.

5.4.1.3.1 Technical description. This specification describes boiler water testing chemicals including Class F - chloride indicator powder, which is composed of 0.250 ± 0.038 g of diphenylcarbazone and 0.020 ± 0.003 g of crystalline bromophenol blue, contained in a gelatin capsule. Indicator solution for test is prepared by dissolving the contents of a capsule in 95% ethyl alcohol to a volume of 50 mL. The performance of the indicator is tested as specified by titration of a sodium chloride solution with a mercuric nitrate solution until the color just changes from yellow to lavender.

5.4.1.3.2 Use. Class F - chloride indicator powder is intended for use as a chloride test indicator solution for titration with mercuric nitrate solution. An indicator solution is prepared by dissolving the contents of a capsule in 50 mL of 95% ethyl alcohol, ACS Reagent, or 50 mL of isopropyl alcohol, ACS, Reagent.

5.5 Reduction-oxidation Indicators. Reduction-oxidation (redox) indicators are highly colored substances that change color when oxidized or reduced. The oxidized form has a different color than the reduced form, and the change is a reversible half-reaction. The oxidation state of the indicator and its color depend on the potential of the solution. A redox indicator appears to be the color of the oxidized form when the concentration of the oxidized form is at least ten times greater than the concentration of the reduced form. The potential of the solution determines the ratio of concentrations of the reduced form to the oxidized form. Conditions for a full color change of a typical indicator are sufficient when the titrant causes a potential change of 0.12 volt for a single electron transfer half-reaction and 0.059 volt for a two electron transfer half-reaction. If the standard potential (Eo) for the indicator is near the equivalence point potential of the titration where there is a rapid change in potential, then the color change occurs at the equivalence point. In general, the action of a redox indicator does not depend upon the specific nature of the oxidant or reductant titrated, but upon the redox potentials of the indicator and of the system titrated. The potential at which a color transition will occur depends on the standard potential for the particular indicator system. Indicators with standard potentials up to about +1.25 volts are available. Table V lists some commercially available redox indicators and their standard potentials (Eo) at pH = 0. The indicators are listed in consecutive order by their potential (volts).

TABLE V
REDOX INDICATORS

COMMON NAME	CHEMICAL NAME	COLOR		POTENTIAL (VOLTS)
		REDUCED FORM	OXIDIZED FORM	
Janus Green B	----	----	----	-0.23
Neutral Red	3-Amino-7-dimethylamino-2-methyl-phenazine Chloride	Colorless	Red	-0.24
----	Dimethylglyoxime(1), ACS	Red	Colorless	0.16
----	N,N-Dimethylindoaniline	----	----	0.22
----	Indophenol, Sodium Salt	Colorless	Blue	0.23
Safranin O	3,7-Diamino-2,8-dimethyl-5-phenyl-phenazinium Chloride	Colorless	Violet	0.24
----	2,3',6-Trichloroindophenol, Sodium Salt	Colorless	Red	0.25
Indigo Carmine	5,5'-Indigosulfonic Acid, Di-sodium Salt	Colorless	Blue	0.29
Nile Blue A	5-Amino-9-(diethylamino)benzo[α]-phenazoxonium Chloride	Colorless	Blue	0.41
Methylene Blue	3,7-Bis(dimethylamino)phenaza-thioniumchloride	Colorless	Blue	0.53
Thionine	3,7-Diaminophenothiazonium Chloride	Colorless	Violet	0.56
----	2,6-Dichloroindophenol, Sodium Salt, ACS	Colorless	Red	0.67
Variamine Blue B Hydrochloride	N-(p-Methoxyphenyl)-p-phenylene-diamine Monohydrochloride	Colorless	Blue	0.71

TABLE V. Continued

COMMON NAME	CHEMICAL NAME	COLOR		POTENTIAL (VOLTS)
		REDUCED FORM	OXIDIZED FORM	
----	3,3'-Dimethoxybenzidine	Colorless	Red	0.76
----	3,3'-Dimethoxybenzidine Dihydrochloride	Colorless	Red	0.76
----	N,N-Dimethyl-p-phenylenediamine	Colorless	Red	0.76
----	Diphenylamine, ACS	Colorless	Violet	0.76
----	N,N-Diphenylbenzidine	Colorless	Violet	0.76
p-Ethoxychrysoidine Monohydrochloride	4-(p-Ethoxyphenylazo)-m-phenylenediamine Monohydrochloride	Red	Violet	0.76
----	p-Diphenylaminesulfonic Acid, Sodium Salt, ACS	Colorless	Violet	0.85
----	Barium Diphenylaminesulfonate	Colorless	Violet	0.85
o-Tolidine(1)	3,3'-Dimethylbenzidine	Colorless	Blue	0.87
----	2,2'-Bipyridine	Red	Blue	0.97
Xylene Cyanole FF	----	Yellow-Green	Pink	1.00
----	N-Phenylanthranilic Acid	Colorless	Pink	1.08
Bathophenanthroline-disulfonic Acid, Disodium Salt	4,7-Diphenyl-1,10-phenanthroline-x,x-disulfonic Acid, Disodium Salt(2)	----	----	1.09
Bathophenanthroline	4,7-Diphenyl-1,10-phenanthroline(1)	----	----	1.13
o-Phenanthroline	1,10-Phenanthroline(1)	Dark Red	Pale Blue	1.14

TABLE V. Continued

COMMON NAME	CHEMICAL NAME	COLOR		POTENTIAL (VOLTS)
		REDUCED FORM	OXIDIZED FORM	
----	1,10-Phenanthroline Monohydrochloride(1)	Dark Red	Pale Blue	1.14
Ferroin	Tris(1,10-phenanthroline)iron(II) Sulfate Solution	Red	Blue	1.14
----	5-Nitro-1,10-phenanthroline(1)	Red	Pale Blue	1.25
----	2,2':6'2"Terpyridine(1)	Red	Pale Blue	1.25
----	Dicyanobis(1,10-phenanthroline)iron	Red	Blue	1.41
Brucine	----	Colorless	Red	----
Methyl Red Hydrochloride,(3) ACS	o-[[p-(Dimethylamino)phenyl]azo]-benzoic Acid Hydrochloride	Violet or Yellow	Orange	----

(1)Fe(II) Present
(2)Fe(II) Present in 1.0M H_2SO_4
(3)Irreversible

5.5.1 Specification for reduction-oxidation indicators.

5.5.1.1 Chemicals, Analytical; General Specification For - Federal Specification O-C-265. The following reduction-oxidation indicators are covered by this specification:

2,6-Dichloroindophenol, Sodium Salt (ACS)
Diphenylamine (ACS)
Diphenylaminesulfonic Acid, Sodium Salt (ACS)
1,10-Phenanthroline (ACS)

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