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NBS MONOGRAPH 54

# **Analytical Standards For Trace Elements In Petroleum Products**



**U.S. DEPARTMENT OF COMMERCE  
NATIONAL BUREAU OF STANDARDS**

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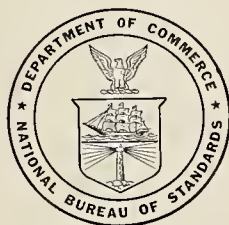
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# Analytical Standards for Trace Elements in Petroleum Products

H. S. Isbell, R. Stuart Tipson, J. L. Hague, B. F. Scribner,  
W. Harold Smith, Clarence W. R. Wade, and Alex Cohen



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# Analytical Standards for Trace Elements in Petroleum Products<sup>1</sup>

H. S. Isbell, R. Stuart Tipson, J. L. Hague, B. F. Scribner, W. Harold Smith,<sup>2</sup>  
Clarence W. R. Wade, and Alex Cohen

A search has been conducted for stable, oil-soluble, organic compounds of metals (and other elements) for use in the spectrographic analysis of petroleum products. Compounds having suitable physical properties have been selected as standards in the determination of the following 24 elements: aluminum, barium, boron, cadmium, calcium, chromium, cobalt, copper, iron, lead, lithium, magnesium, manganese, mercury, nickel, phosphorus, potassium, silicon, silver, sodium, strontium, tin, vanadium, and zinc. The compounds have been purified and analyzed, and are available as certified standards.<sup>3</sup>

These stable, oil-soluble standards were selected from over 150 prospective compounds described in the Monograph. Methods are given for preparation of the compounds and for the spectrographic and chemical analysis of the chosen standards. Procedures are described for the preparation of stable solutions thereof in petroleum oils. Xylene, together with 2-ethylhexanoic acid, 6-methyl-2,4-heptanedione, and 2-ethylhexylamine (and specified mixtures thereof) are used as additives to render the various samples soluble. The resulting solutions are all compatible with each other, so that blends containing a known amount of each element of interest can be prepared as needed.

## 1. Introduction

### 1.1. Origin and History of the Project

Technological advances in the petroleum industry during the past 15 years have occasioned a need for quantitative determination of metallic and other constituents present in petroleum and related products. For example, spectrographic determination of the content of certain elements in lubricating oils after use of the oils in engines provides a simple means for judging engine wear and serves as a guide in maintaining the equipment in a satisfactory operating condition. The research laboratories of petroleum companies have devoted much attention to developing spectrographic methods for determination of trace elements in petroleum products, but have been handicapped by a lack of suitable, pure, oil-soluble compounds (containing the elements of interest) that could be used as standards.

Recognizing the need for standards for instrumental and chemical analysis for metals and other elements in petroleum products, the Committee on Analytical Research, Division of Refining, American Petroleum Institute, proposed that the National Bureau of Standards develop and distribute a series of reproducible, stable, nonvolatile, oil-soluble compounds (preferably solid) suitable for use as analytical, spectrographic standards.

As the result of informal conferences and correspondence, the Committee on Analytical Research prepared an outline of the work desired and made a contract with the Chemistry Division of the National Bureau of Standards for the development of a series of 24 such analytical standards containing, respectively, aluminum, barium, boron, cadmium, calcium, chromium, cobalt, copper, iron, lead, lithium, magnesium, manganese, mercury, nickel, phosphorus, potassium, silicon, silver, sodium, strontium, tin, vanadium, and zinc. These standards were to be distributed under the NBS standard-materials program.

### 1.2. Outline of the Problem

Certain trace elements are present in petroleum products, as residues from crudes carried over in the refining process or as constituents of materials added to improve the lubricating properties or to lessen corrosive effects or oxidation. For many years, analytical chemists in the petroleum industry have had the problems of (a) determining minor elements, particularly metals, in petroleum and (b) establishing the accuracy and reliability of their methods. The analysis usually involves the addition of an accurately known amount of an oil-soluble compound of the element in question to an oil which contains none of this element; the resulting standard solution is carried through all the steps of the method and the amount of the element added is determined. The same procedure is applied to the "unknown" oil, and its content of the element is determined by comparison.

<sup>1</sup> This Monograph is based on work partly supported by the Committee on Analytical Research, Division of Refining, American Petroleum Institute.

<sup>2</sup> Deceased, May 14, 1959.

<sup>3</sup> These standard samples, prepared in solid form for easy weighing and handling, may be purchased for \$10.00 per 5 g of material. A certificate of analysis, plus directions for preparing a solution of the substance, is distributed with each sample. Orders should be directed to the Standard Samples Clerk, National Bureau of Standards, Washington 25, D.C.



The problem of finding suitable metallo-organic compounds for use as standards has increased as more additives have been introduced and as a more exact knowledge of the trace constituents of petroleum and related products has been needed. However, the commercial metallo-organic compounds available were found to be not completely satisfactory as standards because (1) metallic and other contaminants are often present in these compounds in amounts greater than that of the trace element to be determined in the petroleum product; (2) some of the compounds are not sufficiently soluble in petroleum products; (3) some of the compounds are sufficiently volatile that considerable loss occurs during (or even before) the analysis; and (4) when combinations of the elements (as their respective compounds) were dissolved in a single oil, the compounds often gave incompatible mixtures.

In 1955, the Committee on Analytical Research, Division of Refining, American Petroleum Institute realized that the development of suitable standards for chemical analysis and for analysis by emission spectrography, X-ray fluorescence, flame photometry, or colorimetry was a pressing need. A survey revealed that 24 elements, mainly metals, were of particular interest in the analysis of crudes, charge stocks, and finished petroleum products.

### 1.3. Outline of the Project

When this project was started, oil-soluble naphthenates, sulfonates, or hexanoates of most of the metals of interest were available, as were compounds of boron, phosphorus, and silicon. However, few of these were spectroscopically pure, many were unstable under conditions of use, and most of them were unsuitable as standards for analytical determinations. Moreover, methods for the preparation of the pure compounds were unavailable.

Although certain naphthenates and petroleum sulfonates had been used as standards, naphthenic

acids and petroleum sulfonic acids are mixtures having a composition which may differ from batch to batch, and commercial products now available might well differ from materials available in the future. To secure standards that would not differ according to the source, it was decided to prepare a series of more-readily duplicated standards. Consequently, attention was directed to the preparation of definite, reproducible, oil-soluble compounds (preferably solid) of the 24 elements selected by the Committee.

Another object of the project was to develop methods for preparing suitable blends of the standards in an appropriate base oil, so that possession of an adequate collection of oil-soluble compounds would permit preparation of any desired blend (of known concentrations) at any time and make it unnecessary to maintain a variety of standardized blends.

After consultation with the Advisory Committee, the following program was developed.

(1) Tentative selection of general classes of compounds having the desired properties, from indications obtained by a search of the literature and by correspondence with industry.

(2) Qualitative examination of available materials to ascertain their suitability for use as standards.

(3) Preparation and purification of potentially useful compounds.

(4) Determination of pertinent properties of potentially useful compounds.

(5) Selection of specific compounds for use as standards.

(6) Development of methods for preparing oil solutions of the standard compounds.

(7) Preparation of large batches of the standard compounds.

(8) Spectroscopic and chemical analysis of the standard compounds.

(9) Sale and distribution, through the NBS standard-materials program, of the selected compounds as certified standards for analytical use.

## 2. Discussion of the Work Done

### 2.1. Exploratory Study of Available Compounds

The literature submitted to us by the Project Study Group of the Committee was reviewed, and requests were made to all prospective suppliers of oil-soluble, metallo-organic compounds for information concerning potentially useful compounds that they might be able to supply. About 40 samples of commercial compounds were obtained and preliminary tests were made in order to ascertain whether these might prove suitable for use as standards.

### 2.2. Compounds Prepared and Studied

In order to form an opinion as to the kinds of compounds most likely to be suitable for use as

standards, the chemical literature was studied, a large number of potentially useful compounds were prepared, and qualitative tests of their solubility and stability were made. From the results of these studies, the compounds that seemed most suitable were then selected for further study; these are briefly discussed in the next three sections.

Table 1 lists the *salts* prepared and examined. Those italicized were distributed to cooperators in the petroleum industry, for qualitative evaluation. From the results of these and other tests, the compounds listed in table 2 were selected as the most promising; those italicized were prepared and distributed in 1958 to workers wishing to examine them for possible use as standards.



TABLE 1. *Exploratory study of salts of metals*<sup>a</sup>

Salt of	Al	Ba	Cd	Ca	Cr	Co	Cu	Fe	Pb	Li	Mg	Mn	Hg	Ni	K	Na	Sr	Sn	V	Zn
A. Carboxylic Acids																				
1. Naphthenic acids	X <sup>b</sup>	X		X	X		X	X		X	X <sup>b</sup>									X
2. Cyclohexanebutyric acid	X	X	X	X		X	X	X	X	X	X	X	X	X	X	X	X			X
3. 2-Ethylhexanoic acid	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X			X
4. Palmitic acid	X																			
5. Oleic acid	X				X		X	X												
6. Erucic acid	X	X		X	X	X	X	X		X	X			X	X	X	X		X	
B. Dithiocarbamic Acids																				
1. Diethyl-	X			X	X	X	X	X	X		X	X		X		X			X	X
2. Diisopropyl-	X			X	X	X	X	X	X		X	X		X		X			X	X
3. Dibutyl-	X	X	X	X	X <sup>b</sup>	X	X	X	X	X	X	X <sup>b</sup>	X	X	X	X		X	X	X
4. Diisopentyl-						X		X				X				X			X	
5. Bis(1,3-dimethylbutyl)-						X		X				X				X			X	
6. Dibethyl-						X		X				X		X		X			X	
7. Dicyclobexyl-	X	X		X	X	X	X	X		X	X	X		X		X			X	X
8. Bis(2-ethylhexyl)-	X	X		X	X	X	X	X		X	X	X		X		X			X	X
9. 2-Ethylhexyl-	X				X	X	X	X				X		X		X			X	X
10. Hexadecyl-	X				X	X	X	X	X			X		X		X			X	X
11. Cyclobexyl-		X			X						X					X				X

<sup>a</sup> The symbol X indicates that this salt was prepared; an italic X indicates that a sample of this salt was evaluated by cooperators in the petroleum industries.<sup>b</sup> Oily product which did not crystallize.TABLE 2. *First set of compounds selected as possible standards*<sup>a</sup>

(April 11, 1958)

Element	Compound
1. Aluminum	2-ethylhexanoate
2. Barium	(a) erucate; (b) bis(2-ethylhexyl)dithiocarbamate
3. Boron	(a) tris(2-cyclohexylcyclohexyl) borate; (b) tris(diisobutylcarbinyl) borate
4. Cadmium	dibutylidithiocarbamate
5. Calcium	(a) erucate; (b) 2-ethylhexanoate
6. Chromium	(a) oleate; (b) erucate
7. Cobalt	(a) dibutylidithiocarbamate; (b) bis(2-ethylhexyl)dithiocarbamate
8. Copper	(a) dibutylidithiocarbamate; (b) bis(N-salicylidene-2-ethylhexylamine) chelate
9. Iron	(a) dibutylidithiocarbamate; (b) diisopropylidithiocarbamate
10. Lead	dibutylidithiocarbamate
11. Lithium	(a) erucate; (b) dicyclobexylidithiocarbamate
12. Magnesium	erucate
13. Manganese	(a) cyclohexanebutyrate; (b) oleate
14. Mercury	dibutylidithiocarbamate
15. Nickel	(a) dibutylidithiocarbamate; (b) bis(2-ethylhexyl)dithiocarbamate; (c) bis(N-salicylidene-2-ethylhexylamine) chelate
16. Phosphorus	triphenyl phosphate
17. Potassium	(a) erucate; (b) bis(2-ethylhexyl)dithiocarbamate; (c) dicyclobexylidithiocarbamate
18. Silicon	octaphenylcyclotetrasiloxane
19. Silver	
20. Sodium	(a) erucate; (b) dicyclobexylidithiocarbamate
21. Strontium	erucate
22. Tin	dibutylidithiocarbamate
23. Vanadium	bis(salicylaldehyde oxime) chelate
24. Zinc	dibutylidithiocarbamate

<sup>a</sup> The compounds italicized were evaluated by cooperators in the petroleum industries.

As a result of these tests, the compounds listed in table 3 were selected for further study. (Ultimately, the compounds listed in table 6 were chosen as standards.)

### 2.2.1. Metal Salts of Carboxylic Acids and Dialkylidithiocarbamic Acids

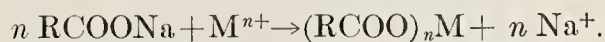
*Salts of carboxylic acids* (see table 1) were prepared by one or other of the following methods.

TABLE 3. *Second set of compounds selected for consideration as standards*

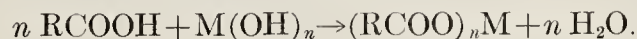
(Sept. 30, 1958)

Element	Compound
1. Aluminum	(a) 2-ethylhexanoate; (b) cyclohexanebutyrate
2. Barium	(a) erucate; (b) 2-ethylhexanoate
3. Boron	menthyl borate
4. Cadmium	(a) dibutylidithiocarbamate; (b) cyclohexanebutyrate
5. Calcium	2-ethylhexanoate
6. Chromium (III)	(a) 2-ethylhexanoate; (b) cyclohexanebutyrate
7. Cobalt (II)	cyclohexanebutyrate
8. Copper	(a) dibutylidithiocarbamate; (b) cyclohexanebutyrate; (c) bis(N-salicylidene-2-ethylhexylamine)
9. Iron (III)	(a) dibutylidithiocarbamate; (b) cyclohexanebutyrate
10. Lead	(a) dibutylidithiocarbamate; (b) erucate
11. Lithium	erucate
12. Magnesium	(a) erucate; (b) cyclohexanebutyrate
13. Manganese	cyclohexanebutyrate
14. Mercury	cyclohexanebutyrate
15. Nickel	(a) bis(2-ethylhexyl)dithiocarbamate; (b) bis(N-salicylidene-2-ethylhexylamine); (c) cyclohexanebutyrate
16. Phosphorus	triphenyl phosphate
17. Potassium	erucate
18. Silicon	octaphenylcyclotetrasiloxane
19. Silver	cyclohexanebutyrate
20. Sodium	(a) erucate; (b) cyclohexanebutyrate
21. Strontium	erucate
22. Tin (IV)	
23. Vanadium	bis(N-salicylidene-2-ethylhexylamine) chelate
24. Zinc	(a) dibutylidithiocarbamate; (b) erucate; (c) cyclohexanebutyrate

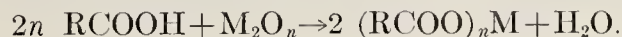
(a) Sodium salt of the acid plus a salt of the metal



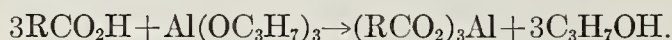
(b) The acid plus the metal hydroxide



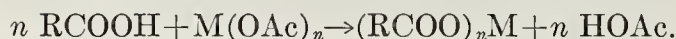
(c) The acid plus the metal oxide



(d) (For aluminum) The acid plus aluminum isopropoxide



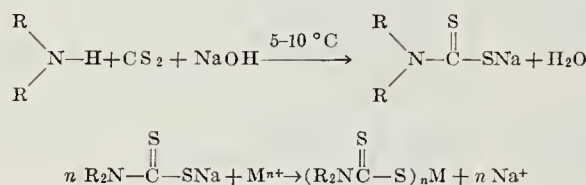
(e) The acid plus the metal acetate



Although the naphthenates were found to have suitable oil-solubilities, they were not chosen as standards because of lack of uniformity of naphthenic acid. In addition to the salts listed in table 1, silver erucate, dibutyltin 2-ethylhexanoate, and silver cyclohexanebutyrate were prepared. The salts of 2-ethylhexanoic acid and cyclohexanebutyric acid were found to be much less soluble than the salts of naphthenic acid, but most of them had the advantage of being definite, reproducible compounds.

Most of the compounds listed in table 1 were obtained as solids, many of them crystalline. Before and after purification, the approximate solubility in such common organic solvents as benzene, xylene, chloroform, alcohol, and ether was ascertained. (This information also served as a guide to the probable degree of solubility in petroleum oils.) For purification of *carboxylic acid salts*, butyl acetate was found to be a general solvent, but chloroform, ethanol, aqueous acetone, and water were preferable in some instances. Acetone was used as a general precipitant for all of the cyclohexanebutyrates.

Many salts of the *dialkyldithiocarbamic acids* were prepared according to the following equations.



where  $\text{M} = \text{Cu}^{++}, \text{Al}^{+++}$ , etc.

Because of their ease of preparation, low solubility in water, and characteristic colors, these salts have been extensively used as organic reagents for the detection and quantitative estimation of many metals. Their solubilities in paraffin or lubricating oils have not, however, been recorded in the literature.

Some of these salts lack stability, but others seemed promising. In general, the heavy-metal salts are insoluble in water but soluble in such low-polarity solvents as benzene, chloroform, carbon tetrachloride, and carbon disulfide. Benzene, chloroform, and ethanol were satisfactory solvents for recrystallization.

The salts of diethyldithiocarbamic acid crystallize readily, but are only slightly soluble in hot paraffin oil. The salts of dicyclohexyldithio-

carbamic acid also have low solubility in paraffin oil. The salts of dibutyldithiocarbamic acid are more soluble; crystalline dibutyldithiocarbamates of cadmium, cobalt, copper, iron, lead, mercury, nickel, and zinc were prepared and found to have many desirable properties, but salts of the other metals were less satisfactory. Salts of bis(2-ethylhexyl)dithiocarbamic acid have excellent solubility, but are much more difficult to isolate and purify than the salts of the other carbamic acids mentioned; only the nickel salt was satisfactory. In addition to the salts listed in tables 1, 2, and 3, some salts of 1,1,3,3-tetramethylbutyldithiocarbamic acid were prepared, but their properties were unsuitable.

The solubility of dialkyldithiocarbamates in lubricating oils is increased by the addition of bis(2-ethylhexyl)dithiocarbamic acid.

## 2.2.2. Chelate Compounds

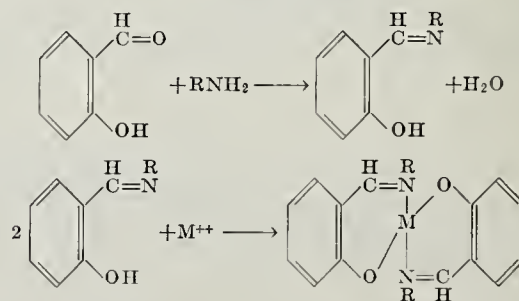
For a given metal, a variety of metallo-organic complexes were prepared and studied, in order to evaluate (1) the methods of preparation; (2) the increase or decrease in solubility caused, in a given class of chelates, by change of the bonding groups and by branching or lengthening of the alkyl side-chain; and (3) the relative stability of various chelates.

Compounds examined in a cursory fashion included metal derivatives of cupferron, dimethylglyoxime,  $\alpha, \alpha$ -(ethylenedinitrilo)di-*o*-cresol, 1-nitroso-2-naphthol, 8-quinolinol, picolinic acid, rhodanilic acid, and the oximes of salicylaldehyde, 1'-hydroxy-2'-acetophenone, and 2'-hydroxyacetophenone.

Compounds prepared and examined in more detail were various metal derivatives of (a) *N*-salicylidenebutylamine and *N*-salicylidene-2-ethylhexylamine, and (b) 1,3-diphenyl-1,3-propanedione, 2,4-hexanedione, 1'-hydroxy-2'-acetophenone, 2'-hydroxyacetophenone, 6-methyl-2,4-heptanedione, 2,4-pentanedione, and 1-phenyl-1,3-butanedione.

### a. Chelate Compounds of Azomethines (Schiff Bases)

The azomethines and their metal complexes were prepared by the following reactions:



where  $\text{R} = \text{alkyl}$ , and  $\text{M}^{++} = \text{a metal ion}$ .

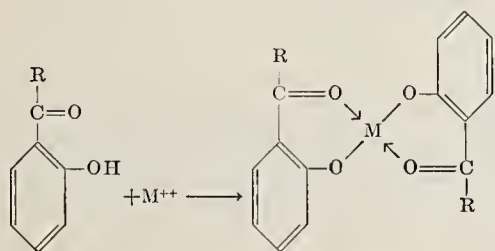
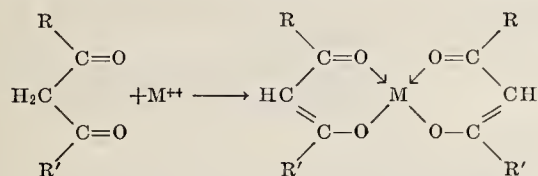
Work was conducted on these chelates of cadmium, cobalt, copper, iron, nickel, vanadium, and zinc. Of these, the crystalline complexes of cop-



per, nickel, and vanadium seemed the most promising. However, the vanadium compounds are not sufficiently stable for use as standards.

#### b. Chelate Compounds of Diketones and Hydroxy Ketones

In general, chelates of the ketones were prepared according to one of the following equations:



where R=H or CH<sub>3</sub>, and R'=alkyl or phenyl.

For aluminum and chromium, liquid chelates of 6-methyl-2,4-heptanedione were prepared [1]<sup>4</sup>; efforts to crystallize these compounds were unsuccessful.

The 2,4-pentanedione chelates of aluminum, cadmium, chromium, cobalt, copper, iron, nickel, and vanadium were prepared; the solubilities of these compounds in lubricating oils were found to be unsatisfactory.

Finally, the 1-phenyl-1,3-butanedione chelates of chromium, cobalt, iron, lead, and vanadium were prepared. Of these compounds, the chelates of cobalt, lead, and vanadium seemed the most promising. Only the vanadium compound was then studied in detail because (a) a suitable vanadium compound had high priority and (b) this diketone is too expensive for consideration unless no other suitable derivative could be found.

#### 2.2.3. Miscellaneous Compounds

A number of miscellaneous compounds were studied.

(a) *Triphenyl phosphate*. A supply of triphenyl phosphate was purchased. The ester was purified by recrystallization from ethanol and from aqueous ethanol, and its solubilities were studied. A spectrographic analysis of the material indicated that it would make a satisfactory standard.

(b) *Borates*. 2-Cyclohexylcyclohexyl borate was prepared. It was found to contain impurities that separated from solutions of the material in oil. Since the impurities were not readily removed, other borates were examined. Menthyl borate was prepared, and it was found to have satisfactory solubility in lubricating oils.

(c) *Octaphenylcyclotetrasiloxane*. Use of this compound as a standard for silicon was suggested

by E. G. Tajkowski of the Silicone Products Department, General Electric Company, Watford, N.Y., and he kindly supplied the material tested. The sample was found to be exceptionally pure and to be suitable for use without further treatment. It had certain desirable properties, but low solubility in lubricating oils.

(d) *Other compounds* studied included ferric 2-methylpentanoate, mercuric 2-methylpentanoate, aluminum 2-ethylhexanoate, calcium 2-ethylhexanoate, iron 2-ethylhexanoate, silver 2-ethylhexanoate, and potassium erucate.

### 2.3. Evaluation of Compounds

#### 2.3.1. Cooperative Tests

In the evaluation of samples of our compounds in laboratories of the petroleum industries, the following were the cooperative tests made and the cooperators.

*Solubility, stability, and compatibility*. California Research (R. L. LeTourneau), Esso Research and Engineering (H. L. Leland), Gulf Research (R. O. Clark), Phillips Petroleum (B. J. Heinrich), Shell Development (E. D. Peters), Standard Oil of Indiana (E. B. Tucker), Texaco Research (F. M. Roberts), Union Oil (G. R. Lake).

*Volatility*. E. I. du Pont de Nemours (G. H. Patterson), Ethyl Research (C. M. Gambrill).

At the meeting of our group with the Advisory Committee on January 16, 1959, the following decisions were then reached:

(1) To discontinue study of salts of naphthenic acid, because the acid is a variable mixture of acids that may differ from batch to batch.

(2) To avoid use of dithiocarbamates, because, in some projected uses of the standards, introduction of sulfur would be undesirable, particularly in X-ray fluorescence studies.

(3) To continue study of salts of cyclohexanobutyric acid (in preference to salts of erucic acid and 2-ethylhexanoic acid), because they are more readily isolated as solid materials.

(4) To continue search for a suitable compound of vanadium.

(5) To proceed with preparation of large batches of compounds selected as standards, and to purify, analyze, and issue them as provisional standards.

These decisions were then acted on. In connection with *item 4*, bis(1-phenyl-1,3-butanediono)-oxovanadium (IV) was prepared, tested, and selected as the vanadium standard.

#### 2.3.2. Spectrographic Analysis

Qualitative tests on the compounds prepared during the exploratory part of the project indicated that there would be no particular difficulty in obtaining reasonably pure materials for use as standards. After the program had become restricted to products to be used as standards, semiquantitative spectrographic measurements

<sup>4</sup> Figures in brackets indicate the literature references at the end of this Monograph.



(and chemical analyses) were made on a sample taken from the final, highly purified batch of each standard compound. The procedure for, and results of, spectrographic analysis of the standard compounds are given in section 3.6.

### 2.3.3. Chemical Analysis

Each standard sample was analyzed by appropriate methods, the details of which are given in section 3.7. Table 4 lists the various methods employed for decomposing the standard samples, prior to analysis. The analytical results are given in table 6.

TABLE 4. *Methods used for decomposition of standard samples*

Method	Standard Sample No. <sup>a</sup>
Sulfuric-nitric acids-----	1050, 1051, 1052, 1052a, 1053, 1054, 1056, 1056a, 1057, 1057a, 1058, 1059, 1060, 1061, 1061a, 1062, 1062a, 1065, 1065a, 1066, 1067, 1070, 1071, 1072, 1073, 1075.
Ignition-----	1050, 1051, 1051a, 1052, 1052a, 1054, 1055, 1055a, 1056, 1058, 1059, 1059a, 1060a, 1061, 1062, 1065, 1067, 1068, 1069, 1069a, 1070, 1070a, 1073, 1073a, 1074, 1075, 1076, 1077
Peroxide fusion-----	1063, 1063a
Extraction with chloroform----	1064
Perchloric-nitric acids-----	1071a

<sup>a</sup> The name of each standard sample is given in table 6. The letter a after the number of a standard sample indicates material obtained in a second, large-scale preparation.

### 2.3.4. Weight-stability of Standard Compounds

The weight-stability of each standard sample was determined by (a) exposing the sample to an atmosphere of 75 percent humidity for various periods of time, and then, after equilibrium had been reached, (b) drying the same sample over phosphorus pentaoxide. From the results, the drying times recommended in table 5 were obtained.

For those compounds which require only a 2-hr drying time, the maximum gain in weight on exposure to 75 percent humidity was 0.08 percent. The maximum loss in weight when these compounds were then dried over phosphorus pentaoxide was 0.05 percent.

From the results of this work, it is recommended that all specimens of the standard samples should be stored in closed containers in desiccators containing phosphorus pentaoxide.

### 2.3.5. Dissolution in Petroleum Oils

Since most of the solid, metallo-organic compounds that are stable in humid air are, for the intended use, too insoluble in lubricating oil, and since simple methods of dissolving these substances to give stable solutions had not been discovered, it had (before this project was undertaken) been customary to prepare oil solutions of the various compounds without isolating the solids.

TABLE 5. *Time recommended for drying over phosphorus pentaoxide at room temperature*

Time	Standard Sample No. <sup>a</sup>
0-----	1066
2-----	1050, 1052a, 1056, 1056a, 1057, 1057a, 1059a, 1063, 1063a, 1064, 1071, 1071a, 1076, 1077
24-----	1051, 1051a, 1055, 1058, 1060, 1060a, 1068, 1070, 1070a, 1073
48-----	1053, 1054, 1055a, 1059, 1061, 1061a, 1062, 1065, 1065a, 1069, 1069a, 1072, 1073a, 1074, 1075
72-----	1062a

<sup>a</sup> See footnote a to table 4.

However, use of solid materials, which may be conveniently dried, handled, and weighed, is advantageous. Nevertheless, successful application of the set of solid compounds we have developed is contingent on a simple reproducible method of preparing stable solutions of them in petroleum oils.

In many instances, application of heat causes the compound to dissolve in oil, but, on cooling to room temperature and standing for several days, gellation or precipitation often occurs in the solution.

For preparing stable oil-solutions containing the desired concentration of the respective element, several organic solubilizing agents were developed. These could be used in small proportions, and proved satisfactory for preparing single solutions or blends of the 24 metallo-organic standards. These agents may be loosely classified on the basis of their chemical properties and according to the types of compound they solubilize.

Xylene, which has a rather low volatility (high boiling point) was found to be satisfactory for predissolving the selected compounds of boron, phosphorus, silicon, and tin, and it was used, in combination with the other solubilizing agents found necessary, for predissolving all of the standard compounds.

Oil-soluble organic acids, especially naphthenic acid and 2-ethylhexanoic acid, were found to be excellent agents for dissolving the salts (soaps) of lead, manganese, mercury, nickel, zinc, and the alkali and alkaline-earth metals. To maintain compatibility of blends, it was found advisable to employ 2-ethylhexanoic acid with many of the non-soaps. Use of naphthenic acid was discontinued because of variability of the material.

2-Ethylhexylamine was found to solubilize salts of metals that form complexes with ammonia, for example, the salts of cadmium, cobalt, copper, nickel, and silver. Even in daylight, the oil solutions of silver formed in this way are stable for months. In order to stabilize solutions of vanadium for long periods of time, addition of 2,2'-diethyldihexylamine proved satisfactory.



6-Methyl-2,4-heptanedione gives metal derivatives that are difficult to crystallize, and it was found excellent for predissolving the compounds of iron and chromium and for preventing formation of, or dissolving, gels of aluminum salts.

### 3. Experimental Procedures

#### 3.1. Materials

The inorganic salts were reagent or analytical grade. The acetone, chloroform, absolute ethanol, and absolute methanol were reagent grade, and the butyl acetate was commercial material of 90- to 92-percent purity; all organic solvents were used without further purification. Cyclohexanecarboxylic acid (obtained from Distillation Products Industries, Eastman Organic Chemicals Department, Rochester 3, New York) was redistilled, and the fraction boiling at 134 °C (3mm) was collected and used for the preparation of its salts. Scrupulous precautions were taken to avoid contamination of all materials; apparatus was thoroughly cleaned, and dust was removed and excluded.

#### 3.2. Drying of Products

After recrystallization or reprecipitation from an appropriate solvent, each purified product was air-dried overnight (with exclusion of dust), dried in a vacuum desiccator (enclosed in a Desiguard) over phosphorus pentoxide at 0.5 mm, ground with an agate mortar and pestle, and sieved to pass a 40-mesh screen. (For certain hard, noncrystalline, or slightly sticky products, it was necessary first to grind to pass a 20-mesh sieve, redry, and then grind to pass a 40-mesh sieve.) The compound was redried in a vacuum desiccator over phosphorus pentoxide at 0.5 mm, and, if necessary, large quantities were then placed in a rotary cylinder and dried at room temperature at 0.5 mm, under continuous rotation, for at least 48 hr (or until condensate was no longer formed in a dry-ice trap included in the system). Immediately preceding analysis (see sections 3.6 and 3.7), each sample was further dried, as described in section 3.8.

#### 3.3. Preparation of Solubilizing Agents

##### 3.3.1. Bis(2-ethylhexyl)dithiocarbamic Acid

Cold carbon disulfide (7.6 g, 0.1 mole) was added dropwise, with stirring, to 44.3 g (0.2 mole) of cold bis(2-ethylhexyl)amine in an ice bath, at such a rate that the temperature of the mixture did not exceed 10 °C. Stirring was continued for an additional 10 min, after which the reagent was poured into a bottle which was then stoppered. For many of the metallo-organic compounds,

After a compound had been dissolved by use of one or more solubilizers, the solution could be diluted to the desired concentration with lubricating oil or with such hydrocarbons as mineral spirits, paraffin oil, gasoline, or heptane.

dissolution was facilitated by diluting the reagent with an equal volume of xylene.

##### 3.3.2. 6-Methyl-2,4-heptanedione [2]<sup>5</sup>

Anhydrous, ethanol-free sodium ethoxide (2 moles, prepared from 46 g of granular sodium), anhydrous ethyl acetate (352.4 g, 4 moles), and 1 liter of sodium-dried toluene were placed in a 5-liter, 3-necked, round-bottomed flask equipped with a drying tube, a powerful mercury-sealed stirrer, and a 300-ml dropping funnel equipped with a drying tube. The mixture was stirred for 30 min at room temperature, cooled in an ice bath, and vigorously stirred while 4-methyl-2-pentanone (200.3 g, 2 moles) was added slowly over a period of 30 to 60 min. The progress of the reaction was determined by the disappearance of the solid sodium ethoxide.

After the ketone had been added, the mixture was stirred for 3 hr in the ice bath, allowed to stand overnight at room temperature, recooled in an ice bath, and diluted with an equal volume (or more) of cold water to dissolve the solid that had precipitated. After separation of the resulting layers, the aqueous layer was washed with four 100-ml portions of ether, and the toluene layer was extracted with four 100-ml portions of water. The aqueous layer and washings were combined and acidified with 130 ml (65 ml per mole of sodium ethoxide used) of glacial acetic acid, yielding the ketone as the upper, oily layer. This layer was separated, and the lower aqueous layer was extracted with four 100-ml portions of ether. The diketone and the ether extracts were combined, washed successively with three 50-ml portions of water and three 50-ml portions of a saturated solution of sodium bicarbonate, and dried with calcium chloride. The ether was removed by evaporation, and the ketone was fractionally distilled under diminished pressure; yield, 171 g (60 percent), bp, 71–76° C (18 mm).

#### 3.4. Preparation of Compounds Chosen as Standards

Table 6 lists the compounds selected as standards, together with their formulas, molecular weights, and results of analysis for the pertinent element in each.

<sup>5</sup> This compound may now be purchased from Chemicals Procurement Laboratories, Inc., College Point, N.Y.



TABLE 6. *Formulas, molecular weights, and analyses of compounds chosen as standard samples*

Serial No.	NBS Standard Sample No.	Compound	Formula	Molecular weight	Element		
					Symbol	Calculated	Found *
		<i>Cyclohexanebutyrate</i>			%	%	
1	1050	Aluminum	C <sub>20</sub> H <sub>35</sub> AlO <sub>5</sub>	382. 45	Al	7. 05	6. 9
2	1051	Barium	C <sub>20</sub> H <sub>34</sub> BaO <sub>4</sub>	475. 82	Ba	28. 87	28. 1
	1051a						29. 1
3	1053	Cadmium	C <sub>20</sub> H <sub>34</sub> CdO <sub>4</sub>	450. 87	Cd	24. 93	23. 9
4	1054	Calcium	C <sub>20</sub> H <sub>34</sub> CaO <sub>4</sub>	378. 54	Ca	10. 59	10. 5
5	1055	Cobalt (ous)	<sup>b</sup> unknown		Co		17. 1
	1055a						17. 5
6	1056	Copper (ic)	C <sub>20</sub> H <sub>34</sub> CuO <sub>4</sub>	402. 00	Cu	15. 81	16. 0
	1056a						16. 1
7	1058	Iron	<sup>c</sup> unknown		Fe		19. 3
8	1059	Lead	C <sub>20</sub> H <sub>34</sub> O <sub>4</sub> Pb	545. 67	Pb	37. 97	37. 5
	1059a						36. 9
9	1060	Lithium	C <sub>10</sub> H <sub>17</sub> LiO <sub>2</sub>	176. 17	Li	3. 94	4. 0
	1060a						4. 1
10	1061	Magnesium	C <sub>20</sub> H <sub>34</sub> MgO <sub>4</sub>	362. 78	Mg	6. 70	6. 9
	1061a						6. 8
11	1062	Manganese (ous)	C <sub>20</sub> H <sub>34</sub> MnO <sub>4</sub>	393. 40	Mn	13. 97	13. 9
	1062a						13. 8
12	1064	Mercury (ic)	C <sub>20</sub> H <sub>34</sub> HgO <sub>4</sub>	539. 07	Hg	37. 21	36. 2
13	1065	Nickel (ous)	<sup>d</sup> unknown		Ni		17. 6
	1065a						16. 8
14	1067	Potassium	C <sub>10</sub> H <sub>17</sub> KO <sub>2</sub>	208. 33	K	18. 77	19. 0
15	1068	Silver	C <sub>10</sub> H <sub>17</sub> AgO <sub>2</sub>	277. 11	Ag	38. 93	38. 7
16	1069	Sodium	C <sub>10</sub> H <sub>17</sub> NaO <sub>2</sub>	192. 22	Na	11. 96	12. 0
	1069a						11. 9
17	1070	Strontium	C <sub>20</sub> H <sub>34</sub> O <sub>4</sub> Sr•1.5 H <sub>2</sub> O	453. 15	Sr	19. 34	19. 8
	1070a						20. 7
18	1073	Zinc	<sup>e</sup> unknown		Zn		18. 5
	1073a		C <sub>20</sub> H <sub>34</sub> O <sub>4</sub> Zn	403. 84	Zn	16. 19	16. 7
		<i>Miscellaneous</i>					
19	1063	Menthyl borate	C <sub>30</sub> H <sub>57</sub> BO <sub>3</sub>	476. 58	B	2. 27	2. 27
	1063a						2. 4
20	1072	Tris(2'-hydroxyacetophenono)-chromium(III)	C <sub>24</sub> H <sub>21</sub> CrO <sub>6</sub>	457. 41	Cr	11. 37	10. 6
21	1071	Triphenyl phosphate	C <sub>18</sub> H <sub>15</sub> O <sub>4</sub> P	326. 28	P	9. 49	9. 5
	1071a						9. 5
22	1066	Octaphenylcyclotetrasiloxane	C <sub>48</sub> H <sub>40</sub> O <sub>4</sub> Si <sub>4</sub>	793. 21	Si	14. 15	14. 1
23	1057	Dibutyltin bis(2-ethylhexanoate)	C <sub>24</sub> H <sub>48</sub> O <sub>4</sub> Sn	519. 34	Sn	22. 86	23. 6
	1057a						23. 2
24	1052	Bis(1-phenyl-1,3-butanediono)oxovanadium(IV)	C <sub>20</sub> H <sub>18</sub> O <sub>5</sub> V	389. 29	V	13. 09	13. 1
	1052a						13. 1
25	1074	Calcium 2-ethylhexanoate	<sup>f</sup> unknown		Ca		13. 4
26	1075	Aluminum 2-ethylhexanoate	C <sub>16</sub> H <sub>31</sub> AlO <sub>5</sub>	330. 41	Al	8. 17	7. 5
27	1076	Potassium erucate	C <sub>22</sub> H <sub>41</sub> KO <sub>2</sub>	376. 67	K	10. 38	10. 1
28	1077	Silver 2-ethylhexanoate	C <sub>8</sub> H <sub>15</sub> AgO <sub>2</sub>	251. 09	Ag	42. 96	42. 4

a By analysis of the compound dried at 25° over phosphorus pentoxide in a desiccator.

b Calculated for  $C_{20}H_{34}CoO_4$  (M.W., 397.40): Co, 14.83.

c Calculated for  $C_{10}H_{17}O_2Fe(OH)_2$  (M.W., 259.11): Fe, 21.55.

d Calculated for  $C_{20}H_{34}NiO_4$  (M.W., 397.17): Ni, 14.78.

e Calculated for  $C_{20}H_{34}Zn$  (M.W., 403.84): Zn, 16.19.

f Calculated for  $C_{16}H_{30}CaO_4$  (M.W., 326.50): Ca, 10.82.

### 3.4.1. Cyclohexanebutyrates

#### a. Preparation

Table 7 gives a summary of the compounds used in the preparation of the cyclohexanebutyrates and the yields of the respective, purified products.

Aluminum cyclohexanebutyrate (table 6, compound 1) was prepared by the reaction of cyclohexanebutyric acid with aluminum isopropoxide in boiling toluene.

Seven other cyclohexanebutyrates (compounds 5, 7, 9, 13, 14, 16, and 18) were prepared from the free acid (method a). Absolute ethanol (2 liters) was placed in a large Pyrex beaker equipped with an induction-type, electric stirrer, 340.5 g (2 moles) of cyclohexanebutyric acid was added, and the mixture was stirred until all of the acid had dissolved. In some preparations (see table

7), the solution was now heated to 70 to 75 °C on the steam bath. For all salts except that of iron (see detailed description), an aqueous solution of the metal compound (see table 7) at the prescribed temperature was then added dropwise, with stirring, and the preparation was continued as described in the individual descriptions.

This general method was later improved by first converting the cyclohexanebutyric acid to the sodium salt (method b), and this procedure was employed for preparation of the other cyclohexanebutyrates (compounds 2, 3, 4, 6, 8, 10, 11, 12, 15, and 17). Sodium hydroxide (81.6 g of 98 percent; 2.0 moles) was placed in a large Pyrex beaker (equipped with an electric stirrer and 1-liter dropping funnel) and 2 liters of water was added, with stirring. Into the resulting solution was rapidly poured, with stirring, 340.5 g (2.0



TABLE 7. *Experimental details in the preparation of cyclohexanebutyrates*

Starting material				Water used	Temp. <sup>b</sup>	Yield of pure product			Serial No. of product
Formula	Mol. wt.	Amount used				Calcu- lated	Actual		
		<i>g</i> <sup>a</sup>	<i>moles</i>	<i>liters</i>	<i>° C</i>	<i>g</i>	<i>g</i>	<i>%</i>	
Al(OC <sub>3</sub> H <sub>7</sub> ) <sub>3</sub>	204.3	136.2	0.66	0.0	-----	255	249	97	1
Ba(OAc) <sub>2</sub>	255.5	268.3	1.05	2.0	60-70	475.8	333	70	2
Cd(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	308.5	308.5	1.0	1.3	25	450.9	334	74	3
Ca(OAc) <sub>2</sub> ·H <sub>2</sub> O	176.2	185.2	1.05	1.9	25	378.5	295	78	4
Co(OAc) <sub>2</sub> ·4H <sub>2</sub> O	249.1	261.6	1.05	1.8	70-75	-----	270	-----	5
CuSO <sub>4</sub> ·5H <sub>2</sub> O	249.7	262.2	1.05	2.3	25	402.0	368	91	6
FeCl <sub>3</sub> ·6H <sub>2</sub> O	270.3	180.2	0.66	0.5	70-75	-----	134	-----	7
Pb(OAc) <sub>2</sub> ·3H <sub>2</sub> O	379.4	417.3	1.1	2.0	60-70	545.7	463	85	8
LiOH·H <sub>2</sub> O	41.96	83.9	2.0	0.965	25	352.3	314	89	9
Mg(OAc) <sub>2</sub> ·4H <sub>2</sub> O	214.5	214.5	1.0	0.5	25	362.8	287	79	10
MnCl <sub>2</sub> ·4H <sub>2</sub> O	197.9	197.9	1.0	1.0	25	393.4	315	80	11
Hg(OAc) <sub>2</sub>	318.7	334.6	1.05	2.0	25	539.1	380	70	12
Ni(OAc) <sub>2</sub> ·4H <sub>2</sub> O	248.9	261.4	1.05	2.5	70-75	-----	312	-----	13
KOH	56.1	<sup>c</sup> 132.0	2.0	0.449	25	416.6	358	86	14
AgNO <sub>3</sub>	169.9	356.8	2.1	6.0	25	554.2	520	94	15
NaOH	40.0	<sup>d</sup> 81.6	2.0	0.72	25	384.5	322	84	16
SrCl <sub>2</sub> ·6H <sub>2</sub> O	266.6	266.6	1.0	0.5	25	453.2	354	78	17
Zn(OAc) <sub>2</sub> ·2H <sub>2</sub> O	219.5	219.5	1.0	2.0	25	-----	355	-----	18

<sup>a</sup> Per 2.0 moles (340.5 g) of cyclohexanebutyric acid.<sup>b</sup> Of reaction and, unless otherwise noted, of the aqueous solution.<sup>c</sup> Of 85 percent.<sup>d</sup> Of 98 percent.

moles) of warm, molten cyclohexanebutyric acid, and the mixture was stirred until an essentially clear solution resulted (4 min). In some preparations (see table 7), the solution was now heated to 65 to 70° on the steam bath. An aqueous solution of the metal compound (see table 7) at the prescribed temperature was then added dropwise, with stirring, usually during 20 to 30 min, and the preparation was continued as described in the individual descriptions.

(1) *Aluminum cyclohexanebutyrate*. Aluminum isopropoxide (204.3 g, 1 mole), cyclohexanebutyric acid (512.4 g, 3.01 moles), and 1 liter of toluene were placed in a 3-liter, 2-necked, round-bottomed flask fitted with a 1-liter dropping funnel (filled with toluene) and with a reflux condenser to the top of which was attached a connecting tube equipped with a thermometer and a water-cooled condenser set for distillation. The mixture was refluxed for 1 hr; the flow of water through the reflux condenser was then stopped and the water was drained out, the temperature of the heater was regulated to give a reflux ratio of about 1:7, and the stopcock of the dropping funnel was carefully opened and so adjusted that the number of drops of toluene entering the flask equaled the number of drops of distillate collected. During 3 hr, the vapor temperature rose from 80 to 88° and 400 ml of distillate was collected; during a total time of 5 hr, the temperature rose to 110° and 900 ml of distillate was collected (and discarded).

The hot solution was filtered through toluene-washed, filter-paper pulp, and the filtrate was cooled to room temperature, transferred to a 6-liter, Pyrex jar, and vigorously stirred while 4 liters of acetone was gradually added, producing a turbid solution. Stirring of the solution was continued during 30 min, while 1 liter of acetone containing 18 g of water was added, precipitating a white, spongy product. The mixture was

refrigerated overnight, and the precipitate was collected on a Büchner funnel, washed with acetone, and dried and powdered in the usual way.

(2) *Barium cyclohexanebutyrate*. By use of method b and the quantities of reactants given in table 7, a sticky, soft precipitate resulted. After the mixture had been stirred for about 30 min at 60 to 70 °C, the solution was decanted from the precipitate and discarded; the precipitate was washed successively with four 300-ml portions of water at 60 to 70 °C, and two 300-ml quantities of absolute ethanol at 25 °C, and then stirred with 500 ml of acetone for 30 min, during which time the precipitate became hard and granular. The solid was collected on a Büchner funnel, air dried, and dissolved in a hot solution of 600 ml of methanol and 50 ml of water in 2.5 liters of butyl acetate. The hot, clear solution was filtered transferred to a 4-liter beaker (placed on a cork mat and equipped with a stirrer), and allowed to cool while being rapidly stirred. After the solution had been stirred for about 30 min, the barium salt began to separate as a finely divided precipitate; when the temperature of the solution had reached about 25 °C, the precipitate was collected by suction filtration. The filtrate was refrigerated overnight, affording a second batch of precipitate which was collected, combined with the first batch, and air dried. A second purification of the salt was carried out by redissolving in the butyl acetate-methanol-water mixture and cooling, after which the salt was collected on a Büchner funnel, and dried and powdered as usual.

(3) *Cadmium cyclohexanebutyrate*. To a solution of the acid (see table 7) in 667 ml of absolute ethanol was added a solution of the sodium hydroxide (see method b) in 667 ml of water, followed by the solution of cadmium nitrate; a white precipitate was obtained. After being stirred for a further 30 min, the mixture was filtered by



suction, and the precipitate was washed by stirring with water, refiltering, and repeating the process twice. The moist precipitate was added to boiling absolute methanol (in the ratio of 500 g of precipitate to 2 liters of methanol) and the resulting suspension was filtered. The insoluble precipitate remaining was dissolved by suspending it in hot methanol and adding, with stirring, sufficient cyclohexanebutyric acid to give complete dissolution. The two solutions were combined, water was added to turbidity, and the solution was refrigerated, giving a precipitate which was removed with suction. The product was recrystallized as previously described, but excess water was added to the heated solution whenever an oil (instead of crystals) settled out on refrigeration. The product was filtered off, and dried and powdered in the usual way.

*Analysis.* Calculated for  $C_{20}H_{34}CdO_4$ : C, 53.28; H, 7.6. Found: C, 53.35; H, 7.7.

(4) *Calcium cyclohexanebutyrate.* The calcium acetate solution (see table 7) was added to a solution of the sodium cyclohexanebutyrate (see method b) in 700 ml of water plus 700 ml of absolute ethanol; a white precipitate was formed. The mixture was refrigerated overnight; the precipitate was then collected in a Büchner funnel, transferred to a 4-liter beaker (equipped with a stirrer), and washed by stirring with several 200-ml portions of water. The solid was collected by suction filtration, air dried, crushed, and dried over phosphorus pentoxide; weight, 372 g. The dry salt (372 g) was dissolved, with stirring, in a sufficiency of 43:57 (vol/vol) aqueous ethanol at 70 to 75 °C on the steam bath, filtered, cooled to 25 °C, and refrigerated overnight. The salt separated as short, needlelike crystals which were collected by suction filtration and washed with water. The salt was recrystallized once by the same procedure, and dried and powdered as usual.

(5) *Cobalt cyclohexanebutyrate.* By use of method a and the quantities of reactants given in table 7, a soft, lavender precipitate was obtained. After the mixture had been stirred for about 30 min at 65 to 70 °C, the supernatant solution was decanted and discarded, and the precipitate was stirred with 500 ml of acetone for 20 min, during which time the precipitate solidified. The solid was collected by suction filtration, washed successively with water and acetone, and dissolved at 60 to 70° in 1.5 liters of 1:1 (vol/vol) methanol-butyl acetate. The hot solution was filtered through absorbent cotton, cooled to 45 °C, stirred while acetone was added dropwise to incipient turbidity, cooled to 25 °C, and refrigerated. The salt separated as a finely divided precipitate which was collected on a Büchner funnel, washed with absolute ethanol, air dried, repurified (by the same procedure) from 1.2 liters of 1:1 (vol/vol) methanol-butyl acetate, and dried and powdered as usual.

(6) *Copper cyclohexanebutyrate.* A solution of the sodium cyclohexanebutyrate (see method b)

in 4 liters of water plus 1 liter of absolute ethanol was added dropwise to the solution of copper sulfate (see table 7); a finely divided, blue precipitate resulted. The mixture was kept at 25 °C overnight; the precipitate was then collected by suction filtration, transferred to a 4-liter beaker equipped with a stirrer, and washed successively, with stirring, with three 300-ml portions of water, two 300-ml quantities of 50-percent (vol/vol) aqueous ethanol, and 500 ml of acetone (for 20 min). The solid was collected on a Büchner funnel, air dried, powdered, sieved (20-mesh), and dried over phosphorus pentoxide at 2 mm; weight, 398 g. The copper cyclohexanebutyrate (398 g) was dissolved, with stirring, in 1 liter of absolute ethanol at 65 to 70 °C on the steam bath. The hot, blue solution was filtered through filter-paper pulp, and the filtrate was cooled to room temperature and refrigerated. After the solution had been refrigerated for 3 days (with intermittent scratching of the sides of the flask and warming of the solution to 25 °C), the copper salt precipitated from solution. A second purification of the salt was carried out by redissolving the precipitate in 1 liter of absolute ethanol, refrigerating, and nucleating the solution. The salt was collected on a Büchner funnel, and dried and powdered in the usual way.

(7) *Iron cyclohexanebutyrate.* To a solution of the acid (see table 7) in 333 ml of absolute ethanol at 25 °C was added 134 ml of concentrated ammonium hydroxide (sp gr 0.90) and then, with vigorous stirring, the hot solution of ferric chloride. A red-brown oil was precipitated. The supernatant liquor was decanted and set aside, and the oil was transferred to a 2-liter separatory funnel, washed with four 200-ml portions of hot water (70 to 80 °C), filtered twice (with difficulty) through absorbent cotton, and transferred to a 4-liter beaker equipped with a stirrer. Aqueous acetone (2 liters of 10-percent) was gradually added during 30 min, with the formation of a brown granular precipitate which was dissolved in a solution of 13.5 ml of cyclohexanebutyric acid in 667 ml of chloroform and vigorously stirred while 2.7 liters of acetone was added dropwise during 50 min. The solid was collected on a Büchner funnel, washed successively with absolute ethanol and acetone, and dried and powdered as usual. [The filtrate was concentrated and unreacted cyclohexanebutyric acid (213 g, 1.25 moles) was recovered (see section 3.4.1.b).]

(8) *Lead cyclohexanebutyrate.* The hot solution of lead acetate (see table 7) was added to a hot solution of the sodium cyclohexanebutyrate (see method b) in 1.5 liters of water plus 1 liter of absolute ethanol, and a sticky, soft precipitate was produced. The mixture was diluted with 2 liters of water and stirred for 2 hr, during which time the precipitate solidified. The white salt was collected by suction filtration, transferred to a 4-liter beaker, washed successively with three 300-ml portions of water at 60 to 70 °C and two 300-ml quantities of absolute ethanol, and dissolved in 7



liters of butyl acetate at 70 to 80 °C. The hot solution was filtered twice, by suction, through filter-paper pulp on ordinary filter paper, placed in a 10-liter, cylindrical, Pyrex jar, and vigorously stirred while 3 liters of a 2:1 (vol/vol) solution of acetone in butyl acetate was slowly added.

After the solution had been stirred for about 10 min, the lead salt began to separate as a stringy precipitate, and, after about a further 30 min, the suspension became a gel which was too viscous to be stirred. The mass was transferred to a large Büchner funnel, pressed free of most of the butyl acetate, washed with absolute ethanol, and air dried. In like manner, the filtrate (not mixed with the ethanol washings) was stirred until the solution gelled; the butyl acetate solution was pressed out of the precipitate and refrigerated, yielding more precipitate. The precipitates were combined, washed with absolute ethanol, air dried, redissolved in butyl acetate, collected by the same procedure, and dried and pulverized as usual; mp 85–86 °C.

(9) *Lithium cyclohexanebutyrate*. Use of method a and the quantities of reactants given in table 7 gave a solution. The solution was evaporated to 700 ml on the steam bath, and butyl acetate (2 liters) was added to the mixture, which was then heated slowly to 95 to 105 °C until most of the water had evaporated, giving a slightly turbid solution. Sufficient water was added to remove the turbidity, and the mixture was filtered. The filtrate was allowed to cool to room temperature, nucleated, and refrigerated overnight, giving a precipitate which was filtered off with suction and dispersed in 2 liters of butyl acetate. The suspension was heated slowly, with occasional addition of a little water, until the solution showed a slight turbidity at 95 °C. A slight excess of water was added to remove the turbidity, and the clear solution was filtered, cooled, and refrigerated, giving a precipitate which was filtered with suction, washed twice with acetone, and dried and powdered as usual.

(10) *Magnesium cyclohexanebutyrate*. By use of method b and the quantities of reactants given in table 7, a white precipitate was formed. After being stirred for a further 30 min, the mixture was refrigerated overnight. With the aid of a filter-flask containing several ml of butyl acetate (to decrease foaming), the mixture was filtered by suction; the filtrate was refrigerated for 3 to 4 hr (to give a second crop of white precipitate) and refiltered. The precipitates were combined and were washed by stirring with water, refiltering, and repeating the treatment twice.

Butyl acetate (1 liter) was now added to the moist precipitate, and the suspension was slowly heated to 85 to 93 °C and maintained at that temperature until dissolution was complete. (At this point, the solution was often slightly turbid and was boiling gently.) The solution was filtered into a 4-liter beaker, stirred, nucleated, and allowed to cool to room temperature, affording a white precipitate. After the mixture had been

refrigerated overnight, the precipitate was filtered off with suction, again recrystallized from 1 liter of butyl acetate, as before, and dried and powdered as usual.

(11) *Manganese cyclohexanebutyrate*. The solution of sodium cyclohexanebutyrate (see method b) was added to the solution of manganous chloride (see table 7) during 90 min. After being stirred for a further 30 min, the mixture was refrigerated overnight. The suspension was filtered by suction and the precipitate was twice stirred with water and refiltered. The moist product (ca. 2,000 g) was purified as follows. To an aliquot (500 g) was added 143.5 ml of absolute methanol followed by 1,092.5 ml of chloroform, and the suspension was stirred until most of the salt had dissolved. Butyl acetate (1,316 ml) was now added and the mixture was stirred until dissolution was complete. The solution was filtered, and to the clear filtrate was added 865.5 ml of butyl acetate, followed by 108.5 ml of water. The resulting solution was shaken, nucleated, and refrigerated (–5 °C) overnight. The resulting precipitate was filtered off with suction, washed by stirring with acetone and refiltering, and dried and powdered in the usual way.

(12) *Mercuric cyclohexanebutyrate*. The mercuric acetate solution (see table 7) was added to a solution of the sodium cyclohexanebutyrate (see method b) in 1.5 liters of water plus 1 liter of absolute ethanol, giving a milky-white suspension; from this, a very small quantity of heavy oil separated. After the mixture had been stirred for about 15 min, the suspension was refrigerated overnight, giving off-white, sticky crystals which were collected by suction filtration, washed successively (in a 2-liter beaker) with two 200-ml quantities of ice water and one 100-ml portion of absolute ethanol, filtered, and air dried. The crystals were carefully added portionwise to 1.5 liters of vigorously stirred, hot (65 to 70 °C) absolute ethanol containing 20 g of cyclohexanebutyric acid in a 4-liter beaker on the steam bath, and stirring was continued for an additional 5 min, during which time most of the salt dissolved, leaving a deep-orange, insoluble material that was removed completely by three rapid filtrations, with suction, through a layer of filter-paper pulp placed on ordinary filter paper.

The clear filtrate was transferred to a 4-liter beaker equipped with a stirrer, and 40 to 60 ml of water was gradually added, with stirring, to give a faintly turbid solution which was refrigerated overnight. The salt separated as clumps of crystals which were collected by suction filtration, washed with cold absolute ethanol, air dried, recrystallized (by the same procedure) from 1.1 liters of absolute ethanol, and dried and powdered as usual; mp, 75.5–76.5 °C.

(13) *Nickel cyclohexanebutyrate*. By use of method a and the quantities of reactants given in table 7, a viscous, green oil was precipitated.



After the mixture had been stirred for about 30 min at 65 to 70 °C, the supernatant liquor was decanted, and the oil was dissolved in 750 ml of chloroform, transferred to a 3-liter separatory funnel, washed three times with 200-ml portions of water, and filtered twice through absorbent cotton on ordinary filter paper. The clear, green solution was added dropwise, with stirring, to 4 liters of absolute ethanol in a 6-liter cylindrical jar. The salt separated as a finely divided, light-green precipitate which was collected by suction filtration, washed with hot (70 °C), 10-percent (vol/vol) aqueous ethanol, and air dried. The dry product was dissolved in 1 liter of butyl acetate containing 10 g of cyclohexanecarboxylic acid, diluted dropwise with acetone to incipient turbidity, refrigerated, collected on a Büchner funnel, and dried and powdered as usual.

(14) *Potassium cyclohexanecarboxylate*. Using method a, 20-percent aqueous potassium hydroxide solution (see table 7) was added to a solution of the acid in 500 ml of absolute ethanol (faint pink to phenolphthalein). The solution was transferred to a large evaporating dish, concentrated on the steam bath, with frequent stirring, to a volume of about 400 ml, and transferred to an 8-liter beaker equipped with a stirrer. The viscous solution was cooled to 40 °C and stirred, while 5 liters of acetone was added during 15 min, with the formation of a bulky, white, granular precipitate. After the mixture had been stirred for 15 min, the precipitate was collected on a Büchner funnel, washed with acetone, air dried, and mixed with 1.4 liters of 12-percent ethanol-butyl acetate at 60 to 70 °C; 20 to 28 ml of water was added to afford a clear solution. The hot, clear solution was filtered, transferred to a 6-liter beaker, and stirred while enough acetone was added dropwise to form a turbid solution which was then refrigerated overnight.

The salt separated as a soft, soaplike precipitate which was collected by decantation of the supernatant liquor, and washed with 200-ml portions of 5-percent (vol/vol) ethanol-acetone until a finely divided solid was obtained. The filtrate was mixed with more acetone and refrigerated, affording more of the solid product. The precipitates were combined, washed with acetone, air dried, redissolved as before (with the same quantities of solvent), refrigerated, isolated, and dried and powdered as usual.

(15) *Silver cyclohexanecarboxylate*. The silver nitrate solution (see table 7) was added to a solution of the sodium cyclohexanecarboxylate (see method b) in 2 liters of water plus 2 liters of absolute ethanol, and a white precipitate was formed. The mixture was stirred for 30 min; the precipitate was then collected on a large Büchner funnel, pressed free of much of the absorbed liquid, transferred to an 8-liter, cylindrical jar, and washed successively, with stirring, with five 1-liter portions of water, three 1-liter quantities of ethyl alcohol, and 1 liter of acetone (for 15

min). The salt was collected on a Büchner funnel, and dried and powdered as usual.

The silver salt sometimes became dark brown during the preparation and, to remove this color, the following procedure was followed. A suspension of 260 g of dark-brown silver cyclohexanecarboxylate in 300 ml of 30-percent aqueous ethanol in a 4-liter beaker was vigorously stirred while a solution of 20 g of cyclohexanecarboxylic acid in 320 g of concentrated ammonium hydroxide (sp gr 0.90) was slowly added, with the dissolution of most of the solid and the formation of a deep-amber solution. The mixture was filtered; the filtrate was mixed with 4 g of acid-and-water-washed, decolorizing carbon in a 4-liter beaker, heated on the steam bath for 30 min, and filtered twice through filter-paper pulp on ordinary filter paper. Decolorizing carbon (4 g) was added to the filtrate and the process was repeated; the filtrate was then placed in an 8-liter, cylindrical jar (equipped with a stirrer), and stirred while a solution of 20 ml of concentrated nitric acid (sp gr 1.42) and 350 ml of glacial acetic acid in 2 liters of water was added during 45 min, precipitating silver cyclohexanecarboxylate as a bulky, off-white solid. The precipitate was collected on a Büchner funnel, washed with several 500-ml portions of water, pressed free of most of the wash liquid, and dried and powdered as usual; salt recovered, 190 g. This procedure was repeated, if necessary.

(16) *Sodium cyclohexanecarboxylate*. Using method a, a 10-percent aqueous sodium hydroxide solution (carbonate-free; see table 7) was added to a solution of the acid in 500 ml of absolute ethanol (faint pink to phenolphthalein). The solution was placed in a large evaporating dish and, with frequent stirring, was concentrated on the steam bath to a viscous paste to which 200 ml of 1:1 (vol/vol) aqueous ethanol was added, giving a viscous solution. The solution was filtered into a 6-liter beaker equipped with a stirrer, and 1.6 to 2 liters of acetone was gradually added, with stirring, giving a faintly turbid solution which was immediately filtered; the filtrate was refrigerated overnight. The salt separated as long, thin, needlelike crystals which were collected by suction filtration and washed once with 400 ml of 1:3 (vol/vol) ethanol-acetone. A second crop of crystals (about 40 g) was obtained by adding acetone to the filtrate to incipient turbidity and refrigerating the mixture. The salt was recrystallized once by the same procedure, collected, dried, and powdered as usual. During the drying, the crystallinity of the salt was lost.

(17) *Strontium cyclohexanecarboxylate hydrate*. By use of method b and the quantities of reactants given in table 7, a white precipitate was formed. After being stirred for a further 30 min, the mixture was refrigerated overnight. The suspension was filtered by suction and the precipitate was washed by stirring with water, refiltering, and repeating the process twice. Butyl acetate (1



liter) was now added to the moist precipitate, and the suspension was slowly heated to 93 °C and maintained at that temperature until dissolution was complete. (At this point, the solution was boiling.) The solution was filtered through a heated funnel into a 4-liter beaker, and the filtrate was stirred electrically, nucleated periodically, and allowed to cool to room temperature, affording a white precipitate. After the mixture had been refrigerated overnight, the precipitate was filtered off with suction, again recrystallized from 1 liter of butyl acetate, as before, and dried and powdered as usual.

*Analysis.* Calculated for  $C_{20}H_{34}O_4Sr \cdot 1.5 H_2O$ : C, 53.01; H, 8.2. Found: C, 52.77; H, 8.1.

(18) *Zinc cyclohexanebutyrate*. Using method a, a solution of the acid (see table 7) in 1 liter of absolute ethanol was added to the solution of zinc acetate. A white precipitate was formed. After stirring for a further 30 min, the suspension was filtered by suction and the precipitate was washed by stirring with 2 liters of water, refiltering, and repeating the treatment. Butyl acetate (1.334 liters) was now added to the moist precipitate, and the suspension was slowly heated to 70 to 80 °C and maintained at that temperature until dissolution was complete. The solution was filtered, nucleated, and refrigerated overnight, giving a precipitate which was filtered off with suction, again recrystallized from 1.334 liters of butyl acetate, as before, and dried and powdered as usual.

#### b. Recovery of Cyclohexanebutyric Acid

A mixture of impure residues of salts of cyclohexanebutyric acid (crude solids and mother liquors) was placed in a porcelain evaporating dish on the steam bath and the solvents were evaporated. Excess aqueous 50-percent phosphoric acid was added, and the mixture was heated on the steam bath during 72 hr. The resulting aqueous suspension was diluted with water and the free acid was precipitated with ice. (Alternatively, it was extracted with chloroform, and the extract was washed with three portions of water. Decolorizing carbon was added to the washed chloroform layer, and the suspension was heated to boiling and filtered. The brown filtrate was transferred to a porcelain evaporating dish, and the chloroform and water were evaporated on the steam bath.) The resulting moist, crude cyclohexanebutyric acid was rapidly distilled at 3 mm (132–135 °C), and the main fraction of distillate was redistilled twice, giving pure cyclohexanebutyric acid.

#### 3.4.2. Miscellaneous Compounds

(19) *DL-Menthyl borate*. The method of preparation was essentially that described for *l*-menthyl borate [3]. A suspension of 61.8 g (1 mole) of boric acid in a solution of 468.9 g (3 moles) of *DL*-menthol in 2.6 liters of toluene (boiling stone) in a 6-liter, 1-necked, round-bottomed flask (equipped with a Barrett trap and a reflux con-

denser) was boiled until the acid had dissolved (15 min) and for a further 2.75 hr; 53.4 ml of water was collected in the trap (theoretical yield, 54.0 g). The reaction mixture was allowed to cool to room temperature, and the reflux condenser and trap were replaced by a water-cooled condenser arranged for distillation. Two liters of toluene was distilled off and the remaining hot solution was filtered twice, by suction, and refrigerated, yielding 458 g (dry) of colorless crystals. This material was recrystallized twice from 1.5 liters of a 1:1 (vol/vol) solution of acetone in ethyl acetate, and dried and powdered as usual; weight, 434 g (91 percent), mp, 151–152 °C.

(20) *Tris(2'-hydroxyacetophenono)chromium (III)*. 2'-Hydroxyacetophenone (1361.4 g, 10 moles) was dissolved in 2 liters of absolute ethanol in a 4-liter beaker equipped with a stirrer, and vigorously stirred while 900 g of concentrated ammonium hydroxide (sp gr 0.90) was slowly added. The resulting pale-amber solution was stirred while a solution of 954 g of a commercial chromic acetate hydrate (corresponding to 3.0 moles of anhydrous acetate) in 3 liters of water was added, with the formation of a purplish-red solution; this solution was placed in an 8-liter, cylindrical, Pyrex jar and concentrated on the steam bath during 5 days to a sticky, tarry residue. The residue was mixed with 500 ml of absolute ethanol, and the mixture was gently heated on the steam bath while 200 g of concentrated ammonium hydroxide (sp gr 0.90) was added dropwise.

The mixture was reconcentrated to a tarry residue, cooled to 40 °C, and dissolved in 3 liters of chloroform, with the formation of a deep-brown solution which was filtered through filter-paper pulp, transferred to a separatory funnel, and washed with 100-ml portions of water until the aqueous washings were colorless. The chloroform solution was then concentrated to half volume, and stirred while 4 liters of petroleum ether (bp, 38 to 67 °C) was added portionwise during 30 min, with the precipitation of a greenish-tan solid. The solid was collected by suction filtration and washed with petroleum ether; the filtrate was placed in an evaporating dish, concentrated to a paste, dissolved in chloroform, filtered, and treated with petroleum ether as above, affording more solid material. The precipitates were combined, air dried, and dried and powdered as usual; weight, 840 g (61 percent).

(21) *Triphenyl phosphate*. Triphenyl phosphate (technical grade, from Fisher Scientific Co.; 978 g) was dissolved in 2 liters of absolute ethanol in a 6-liter flask (equipped with a stirrer) on the steam bath. The solution was kept at 60 to 70 °C and vigorously stirred while 2 liters of water at 60 °C was gradually added, affording two layers. Most of the upper (aqueous) layer was removed by decantation, and a further 2 liters of water at 60 °C was added, with stirring, to the lower layer. The mixture was transferred to a separatory funnel, and the lower layer was drawn off and cooled,



with stirring, until material crystallized. The crystals were collected on a Büchner funnel, air dried, and dissolved in 2 liters of absolute ethanol in a 5-liter flask on the steam bath. The hot, clear solution was filtered, cooled to room temperature, and refrigerated overnight, giving colorless crystals which were collected by suction filtration. Water was added to the filtrate, to incipient turbidity; on refrigeration, a second crop of crystals was obtained. The two crops were combined, recrystallized in the same way, and dried and powdered as usual; weight, 820 g (84 percent recovery); mp 49–50 °C.

(22) *Octaphenylcyclotetrasiloxane*. This compound was purchased from the Silicone Products Department, General Electric Company, Waterford, New York; it was found to need no further purification or drying.

(23) *Dibutyltin bis(2-ethylhexanoate)*. Commercial dibutyltin bis(2-ethylhexanoate)<sup>6</sup> (2,500 g) was dissolved in 2 liters of absolute methanol in a 6-liter flask on the steam bath. The hot solution was filtered twice, transferred to a 6-liter, Pyrex jar (placed in an ice bath and equipped with a stirrer), and vigorously stirred while precipitation occurred. After the mixture had been stirred for about 2 hr at 5 to 10 °C, the crystals were collected by suction filtration. The filtrate was concentrated to half volume, filtered, and refrigerated overnight, yielding a second crop of crystals that was combined with the first crop and air dried. The compound was recrystallized once by the same procedure, and dried and powdered as usual; weight, 1,868 g (75-percent recovery).

(24) *Bis(1-phenyl-1,3-butanediono)oxo-vanadium (IV)*. This compound had previously been prepared by a different method [4]. 1-Phenyl-1,3-butanedione (324.4 g, 2 moles) was dissolved in 2 liters of absolute ethanol in a 4-liter beaker (equipped with a stirrer) on the steam bath. The solution was maintained at 70 to 80 °C and vigorously stirred while a hot (75°) suspension of 219.1 g (1.1 moles) of vanadyl sulfate dihydrate in 1 liter of water was added rapidly, producing a clear, green solution. After the solution had been heated for 10 min, a solution of 313 g (2.3 moles) of sodium acetate trihydrate in 700 ml of water at 70 to 80 °C was added, with stirring, during 20 min, precipitating a small quantity of green crystals. The mixture was carefully diluted with water to incipient turbidity, refrigerated overnight, diluted with an equal volume of cold water, and refrigerated for 4 hr.

The crystals were collected on a Büchner funnel, washed successively with two 200-ml portions of cold water and two 200-ml portions of cold absolute ethanol, and air dried on the filter. The crude, dry product, weighing 379.4 g, was dissolved in 1.6 liters of chloroform in a 3-liter beaker on the steam bath, and the solution was diluted with 2 liters of absolute ethanol and

transferred to a 5-liter, round-bottomed, one-necked (standard taper, 40/50) flask. The flask was attached to a rotary still by means of a modified adapter, and evaporated at 50° and 5 mm to half volume or until crystals began to separate. The flask was kept in an ice bath for 3 hr, with frequent shaking, and the crystals were collected by suction and washed with cold absolute ethanol; the filtrate was evaporated further in the rotary still, and cooled in an ice bath, affording a second batch of crystals which was collected, combined with the first batch, air dried, recrystallized in the same way, and dried and powdered as usual; weight, 340 g (87 percent), mp 214–215 °C.

(25) *Calcium 2-ethylhexanoate*. A solution of 176.2 g (1 mole) of calcium acetate hydrate in 600 ml of water was slowly added, with stirring, to a solution of 344.4 g (2 moles) of 2-ethylhexanoic acid in 500 ml of 95 percent ethanol that had been neutralized with 10 percent sodium hydroxide (using phenolphthalein as indicator). The clear solution was vigorously stirred and heated on the steam bath, giving a white precipitate which was removed at about 30-min intervals until precipitation was complete. The precipitate was added to 1,500 ml of hot butyl acetate (95–100 °C) and vigorously stirred while sufficient water was added to produce a clear solution. The solution was filtered, allowed to cool to room temperature, and refrigerated overnight, giving a white precipitate which was recovered by suction filtration, again dissolved in butyl acetate, cooled, and reprecipitated. The precipitate was filtered with suction, washed with acetone, dried, and powdered as usual; weight 290 g.

(26) *Aluminum 2-ethylhexanoate*. This compound was prepared according to the procedure given for aluminum cyclohexanebutyrate. From 3 moles of 2-ethylhexanoic acid, 406 g (88.8 percent) of the compound was obtained.

(27) *Potassium erucate*. Aqueous, 5-percent potassium hydroxide solution was added to a solution of 338.6 g (1 mole) of recrystallized erucic acid in 1,500 ml of 95-percent ethanol (faint pink to phenolphthalein). The solution was transferred to a large evaporating dish, concentrated on the steam bath, with frequent stirring, to a thick paste, and transferred to an 8-liter beaker equipped with a stirrer. The paste was mixed with 1 liter of water and stirred while 3 liters of acetone was added during 25 min, with the formation of a bulky, white precipitate. After the mixture had been stirred for a few minutes, the precipitate was collected on a Büchner funnel, washed with acetone, air dried, mixed with 2.5 liters of butyl acetate, and heated (with stirring) to 90–100 °C; sufficient water was added to afford a clear solution. The hot solution was filtered, allowed to cool to room temperature, and refrigerated overnight, giving a fine, granular precipitate which was filtered with suction, washed with acetone, dried, and powdered as usual; weight, 347 g (92 percent).

<sup>6</sup> This compound was obtained from Metal & Thermit Corporation, Rahway, New Jersey, under the trade name of M. & T. Catalyst T-8, Dibutyltin di-2-ethylhexoate.



(28) *Silver 2-ethylhexanoate*. This compound was prepared according to the procedure given for silver cyclohexanebutyrate. From 2 moles (288.4 g) of 2-ethylhexanoic acid, 360 g (91 percent) of the pure, dry salt was obtained.

### 3.5. Other Compounds Investigated

#### 3.5.1. Erucates and 2-Ethylhexanoates

Most of the *erucate salts* were prepared by the addition of an aqueous solution of the metal hydroxide or acetate to an ethanol or acetone solution of the required amount of purified erucic acid [5]. Erucates not prepared by this method were obtained by addition of an aqueous solution of a salt of the desired metal to a warm methanol solution of potassium erucate. This caused the precipitation of crude product; the reaction mixture was then cooled in the refrigerator for several hours, and the product was separated by filtration and washed. The crude salt was triturated in a large beaker with large amounts of water. After thorough extraction, the product was filtered off, air dried, dissolved in hot butyl acetate, the suspension filtered, and the solution cooled slowly. After 18 hr, the product was separated, and washed with a suitable solvent (acetone or methanol). The material was recrystallized several times and then dried in a rotary drier under diminished pressure.

Freshly prepared stannic erucate dissolves in mineral oil, but the salt, on drying and keeping, becomes insoluble and no means has been found for preparing solutions of this dried compound in oils.

The *2-ethylhexanoates* were prepared by procedures analogous to those outlined for the erucates. However, acetone and methanol were ineffective as precipitants for these salts, most of which could only be isolated as oils.

#### 3.5.2. Dialkyldithiocarbamates

The sodium salts of the dialkyldithiocarbamic acids were prepared by slowly mixing a cold, 10-percent, alcoholic solution of the secondary amine with an equimolar quantity of cold carbon disulfide in ethanol and then slowly adding an equimolar quantity of 10-percent aqueous sodium hydroxide, with stirring until all turbidity disappeared.

Ordinarily, the sodium salt was used directly (without isolation) for the preparation of other salts, by mixing its aqueous solution with the calculated quantity of a 10-percent aqueous solution of the appropriate metal salt of an inorganic acid. However, it was observed that, if the sodium dialkyldithiocarbamate is isolated by removal of the solvent, the difficulty encountered in obtaining certain of the salts as solids is greatly lessened.

Most of the salts of the dialkyldithiocarbamic acids crystallize readily and are easily purified by recrystallization from ethanol, or from a mixture

of ethanol and chloroform or benzene.

The preparation of lead dibutyldithiocarbamate is typical of the methods used.

*Preparation of lead dibutyldithiocarbamate*. A 10-percent aqueous solution of lead nitrate (0.05 mole) was added dropwise, with mechanical stirring, to an aqueous solution of commercial sodium dibutyldithiocarbamate (0.1 mole). Crude lead dibutyldithiocarbamate separated as a gum, from which the supernatant liquor was decanted; the product was triturated with large amounts of water, filtered, air dried, dissolved in hot isopropyl alcohol, and the suspension filtered. The filtrate was cooled, and the resulting crystals were filtered off, air dried, and recrystallized in the same way. Cold methanol was used for washing the crystals. Finally, the pure product was dried in a rotary drier at 60 °C and 1 mm; it had mp 78.5–79.0 °C.

#### 3.5.3. Azomethine Chelates

The azomethines were prepared by mixing the aldehyde or ketone with an equimolar quantity of the appropriate amine, using methanol as the solvent. The metal chelate was then prepared by adding an aqueous solution of the inorganic salt to the Schiff base, followed by addition of sodium acetate. The mixture was kept at incipient boiling for about 30 min and left under refrigeration overnight.

The copper, nickel, and vanadium chelates of *N*-salicylidene-2-ethylhexylamine were obtained as crystalline compounds having excellent solubility in oils, but its iron, cobalt, and aluminum chelates were only obtained as oils.

*Preparation of Bis (N-salicylidene-2-ethylhexylamino)oxovanadium (IV)*. To prepare this compound [6], 12.9 g (0.1 mole) of 2-ethylhexylamine was added to a solution of 12.2 g (0.1 mole) of salicylaldehyde in 100 ml of absolute ethanol. The mixture was allowed to stand for about 30 min, and 100 ml of a 5-percent aqueous solution of vanadyl sulfate dihydrate (0.05 mole) was added. After thorough mixing, 50 ml of a 10-percent aqueous sodium acetate solution was added, and the mixture was heated on the steam bath for 30 min. A brown oil was precipitated; it was separated by decantation and washed several times with hot water. Finally, the crude product (about 25 g) was dissolved in 80 ml of ethanol and refrigerated overnight. The green crystals were separated and dried in vacuo over phosphorus pentoxide for 12 hr. The product was recrystallized three times by the same method; yield, 23 g; mp 93–93.5 °C. This compound dissolves readily in bis(2-ethylhexyl)dithiocarbamic acid. The solution is stable for only a few days, but the stability is improved by the addition of naphthenic acid and, possibly, by the addition of 6-methyl-2,4-heptanedione.

Similar complexes of copper and nickel were prepared in the same manner; both of these chelates appeared to have satisfactory solubility in oils.



TABLE 8. Spectrographic analysis of standard samples

Standard Sample No.	Major element	Minor elements	Standard Sample No.	Major element	Minor elements
		%			%
1050	Al	Fe, Si (<0.01)	1063	B	Si (<0.01)
1051	Ba	Sr (<0.1); Ca, Si, Sn (<0.01)	1063a	B	<0.01, of any
1051a	Ba	Sr (<0.1); Ca, Na (<0.01)	1064	Hg	Na, Mg, Si (<0.01)
1052	V	Al (<0.1)	1065	Ni	Cu, Fe (<0.01)
1052a	V	<0.01, of any	1065a	Ni	<0.01, of any
1053	Cd	<0.01, of any	1066	Si	<0.01, of any
1054	Ca	Sr (<0.1); K, Si (<0.01)	1067	K	Na, Sr (<0.1); Ca, Fe, Si (<0.01)
1055	Co	Ni, Sn (<0.1); Al, Cu, Fe, Mn (<0.01)	1068	Ag	Si (<0.01)
1055a	Co	Ni (<0.1); Cu, Si (<0.01)	1069	Na	Al, Si (<0.01)
1056	Cu	Al, Si (<0.01)	1069a	Na	<0.01, of any
1056a	Cu	<0.01, of any	1070	Sr	Ca (<0.1); Ba (<0.01)
1057	Sn	<0.01, of any	1070a	Sr	Ca (<0.1); Ba (<0.01)
1057a	Sn	<0.01, of any	1071	P	<0.01, of any
1058	Fe	Al, Mn, Mo, Si, Sn (<0.01)	1071a	P	<0.01, of any
1059	Pb	Sn (<0.1); Fe (<0.01)	1072	Cr	Ba (<0.1); Al, Si, Sr (<0.01)
1059a	Pb	<0.01, of any	1073	Zn	Ca, Mg, Ni, Si (<0.01)
1060	Li	Ca, Na (<0.1); Al, K, Si (<0.01)	1073a	Zn	<0.01, of any
1060a	Li	<0.01, of any	1074	Ca	Ba, Na, Sr (<0.01)
1061	Mg	Mn (<0.01)	1075	Al	Si (<0.01)
1061a	Mg	<0.01, of any	1076	K	Al, Ca, Mg, Si (<0.01)
1062	Mn	Sr (<0.1); Al, Pb, Mo, Sn (<0.01)	1077	Ag	Si (<0.01)
1062a	Mn	<0.01, of any			

### 3.6. Spectrographic Analysis

Spectrographic analysis was applied in rapid surveys of preliminary and final samples for qualitative or semiquantitative analysis for 50 or more chemical elements. In this procedure, a small sample was volatilized in an electric arc, the spectrum of the arc was photographed, and the spectrogram was examined for the presence of prominent spectral lines of the various elements by comparison with a standard reference spectrum. Semiquantitative estimates of ranges of concentration of the impurities were reported. For the elements found present in significant amounts, quantitative determinations were made subsequently by chemical analysis or by spectrographic analysis relative to synthesized standards.

The detailed procedures and apparatus used for the semiquantitative analyses were as follows. A 5-mg portion of the powdered sample was mixed with 2 mg of high-purity graphite powder, which acted as a buffer to assist in volatilizing the sample. The charge was placed in a graphite electrode (having a shallow cup) and was vaporized and excited in a direct-current arc, with a starting current of 5 amp and a running current of 15 amp. The light from the arc, passing through the slit of the spectrograph, was dispersed into a spectrum and this was photographed in the spectral range from 2,200–4,800 Å on Eastman 33 plates. The spectrograph used for this work employed a Wadsworth mounting of a concave grating which had 15,000 lines per inch and a radius of curvature of 21 ft, and which produced a spectrum with linear, reciprocal dispersion of 5 Å per mm in the first order. In some cases, where greater sensitivity was desired for the alkali metals, the spectrum was also photographed in the range 4,800–7,000 Å, with an Eastman I-N plate.

The elements searched for in all samples included the following: Ag, Al, As, Au, B, Ba, Be, Bi,

Ca, Cd, Ce, Co, Cr, Cu, Fe, Ga, Ge, Hf, Hg, In, Ir, La, Mg, Mn, Mo, Nb, Ni, Os, P, Pb, Pd, Pt, Rh, Ru, Sb, Sc, Si, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn, and Zr. In addition, Cs, K, Li, Na, and Rb were sought in alkali samples, using the special conditions described in the preceding paragraph.

The results of spectrographic semiquantitative analyses of the final materials issued as standard samples are given in table 8.

As a check on the semiquantitative analysis, quantitative spectroscopic analysis was made for impurities in nickel cyclohexanecarboxylate (Standard Sample 1065), using a procedure similar to that of ASTM Tentative Method E129-57T,<sup>7</sup> in which the sample is ignited to form the oxide, and analysis is made by direct-current arc excitation relative to standard samples prepared in oxide form. The results of this analysis, given in percentage of the element in the original metallo-organic compound, are given below.

Cu-----	0.004	Ti	<0.0002
Fe-----	.001	Mo	<.0002
Si-----	<.0006	Al	<.0002
Co-----	<.0004	Mg	<.0002
Cr-----	<.0002		

### 3.7. Chemical Analysis

For each determination, a sample (approximately 1 g) was dried over phosphorus pentoxide for the time recommended in table 5, accurately weighed, and analyzed. All analyses were performed in duplicate, at least. The analytical results are given in table 6.

For decomposition prior to analysis, two methods were mainly employed. For 22 of the standard samples, decomposition was accomplished either by (a) wet-ashing with sulfuric

<sup>7</sup> Methods for Emission Spectrochemical Analysis, 3d ed., pp 139-43 (American Society for Testing Materials, Philadelphia, 1960).



and nitric acids, followed by determination of the element in the solution by appropriate methods, or (b) ignition. For 13 of the compounds, both methods were applied. The residue obtained by ignition was either (a) weighed as the oxide; (b) treated with sulfuric acid and the sulfate weighed; (c) reduced with hydrogen and the metal weighed; or (d) dissolved in acid and the metal determined by various means. However, menthyl borate (Standard Sample 1063) was fused with sodium peroxide, and the organic material of mercuric cyclohexanebutyrate (Standard Sample 1064) was extracted with chloroform. Triphenyl phosphate (Standard Sample 1071a) was decomposed by wet-ashing with perchloric and nitric acids.

The details of the methods of analysis for each standard sample are given in the next four subsections.

### 3.7.1. Wet-ashing; Ignition

*Aluminum cyclohexanebutyrate* (Standard Sample 1050). Aluminum was determined by wet-ashing, precipitating with ammonium hydroxide, and igniting the filtered precipitate to aluminum oxide at 1,100 °C. Determinations were also made by direct ignition of a sample, wrapped in filter paper and covered with oxalic acid, to aluminum oxide at 1,100 °C.

*Barium cyclohexanebutyrate* (Standard Sample 1051). Barium was determined by wet-ashing, filtering the barium sulfate, and weighing it after ignition at 1,000 °C. Determinations were also made by direct ignition of a sample wrapped in filter paper and covered with oxalic acid. The residue was converted into barium sulfate and weighed after ignition at 900 °C.

*Bis(1-phenyl-1,3-butanediono)oxovanadium (IV)* (Standard Sample 1052). Vanadium was determined by wet-ashing, oxidizing the vanadium with nitric acid, and titrating the vanadium with ferrous ammonium sulfate solution. Determinations were also made by direct ignition of a sample wrapped in filter paper and covered with oxalic acid. The oxide was ignited at 800 °C and weighed as vanadium pentaoxide.

*Calcium cyclohexanebutyrate* (Standard Sample 1054). Calcium was determined by wet-ashing, precipitating the calcium sulfate in alcoholic solution, and weighing the calcium sulfate after ignition at 600 °C. Determinations were also made by direct ignition of a sample wrapped in filter paper and covered with oxalic acid. The oxide was converted into calcium sulfate, and weighed after ignition at 700 °C.

*Copper cyclohexanebutyrate* (Standard Sample 1056). Copper was determined by wet-ashing, depositing the copper by electrolysis, and weighing as metallic copper. Determinations were also made by direct ignition of a sample wrapped in filter paper and covered with oxalic acid. The oxide was ignited under hydrogen, and weighed as the metal.

*Ferric cyclohexanebutyrate* (Standard Sample

1058). Iron was determined by wet-ashing, precipitating with ammonium hydroxide, dissolving the precipitate in hydrochloric acid, reducing with stannous chloride, and titrating with potassium dichromate. Determinations were also made by direct ignition of a sample, wrapped in filter paper and covered with oxalic acid, to ferric oxide at 1050 °C.

*Lead cyclohexanebutyrate* (Standard Sample 1059). Lead was determined by wet-ashing, filtering the lead sulfate through a porcelain frit, and weighing the lead sulfate after ignition at 600 °C. Determinations were also made by direct ignition of a sample wrapped in filter paper and covered with oxalic acid. The oxide was dissolved in nitric acid, precipitated with chromate, and weighed as lead chromate after drying at 140 °C.

*Magnesium cyclohexanebutyrate* (Standard Sample 1061). Magnesium was determined by wet-ashing, precipitating twice as magnesium ammonium phosphate, and weighing the magnesium pyrophosphate after ignition at 1,000 °C. Determinations were also made by direct ignition of a sample wrapped in filter paper and covered with oxalic acid. The residue was converted into magnesium sulfate and weighed after ignition at 700 °C.

*Manganous cyclohexanebutyrate* (Standard Sample 1062). Manganese was determined by wet-ashing, oxidizing the manganese with ammonium persulfate, and titrating the manganese with sodium arsenite solution. Determinations were also made by direct ignition of a sample wrapped in filter paper and covered with oxalic acid. The residue was converted into manganous sulfate and weighed after ignition at 700 °C.

*Nickel cyclohexanebutyrate* (Standard Sample 1065). Nickel was determined by wet-ashing, precipitating with dimethylglyoxime, and weighing the nickel dimethylglyoxime precipitate after drying at 150 °C. Determinations were also made by direct ignition of a sample wrapped in filter paper and covered with oxalic acid. The oxide was ignited under hydrogen and weighed as the metal.

*Potassium cyclohexanebutyrate* (Standard Sample 1067). Potassium was determined by wet-ashing, removing the excess acid by evaporation, and weighing the potassium as potassium sulfate after ignition at 650 °C. Determinations were also made by direct ignition of a sample wrapped in filter paper and covered with oxalic acid. The residue was converted either into potassium sulfate or potassium chloride and weighed after ignition at 650 °C.

*Strontium cyclohexanebutyrate* (Standard Sample 1070). Strontium was determined by wet-ashing, precipitating the strontium sulfate in alcoholic solution, and weighing the strontium sulfate after ignition at 600 °C. Determinations were also made by direct ignition of a sample wrapped in filter paper and covered with oxalic acid. The residue was converted into strontium sulfate, and weighed after ignition at 700 °C.



*Zinc cyclohexanebutyrate* (Standard Sample 1073). Zinc was determined by wet-ashing, precipitating with hydrogen sulfide from 0.01 N acid, and igniting the filtered precipitate to zinc oxide at 950 °C. Determinations were also made by direct ignition of a sample, wrapped in filter paper and covered with oxalic acid, to zinc oxide at 950 °C.

### 3.7.2. Wet-ashing

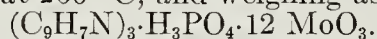
*Cadmium cyclohexanebutyrate* (Standard Sample 1053). Cadmium was determined by wet-ashing, electrodepositing the cadmium from an alkaline cyanide solution, or from 0.5-percent sulfuric acid solution, and weighing the metal.

*Dibutyltin bis(2-ethylhexanoate)* (Standard Sample 1057). Tin was determined by wet-ashing, precipitating the tin with cupferron, and igniting to stannic oxide at 1,000 °C. Determinations were also made by wet-ashing, reducing the tin with metallic nickel, and titrating the tin with potassium iodate solution.

*Lithium cyclohexanebutyrate* (Standard Sample 1060). Lithium was determined by wet-ashing, removing the excess acid by evaporation, and weighing the lithium as lithium sulfate after ignition at 600 °C.

*Octaphenylcyclotetrasiloxane* (Standard Sample 1066). Silicon was determined by wet-ashing, dehydrating the silica twice, igniting the silica at 1,100 °C, and volatilizing the silicon with hydrofluoric acid.

*Triphenyl phosphate* (Standard Sample 1071). Phosphorus was determined by wet-ashing, twice precipitating with magnesia mixture, and igniting to magnesium pyrophosphate at 1,000 °C. Phosphorus was also determined (for Standard Sample 1071a) by wet-ashing with perchloric and nitric acids, precipitating the phosphorus with quinoline in the presence of sodium molybdate, drying the precipitate at 250 °C, and weighing as



*Tris(2'-hydroxyacetophenone)chromium(III)* (Standard Sample 1072). Chromium was determined by wet-ashing, oxidizing the chromium with ammonium persulfate, and titrating the chromium with ferrous ammonium sulfate solution.

### 3.7.3. Ignition

*Cobalt cyclohexanebutyrate* (Standard Sample 1055). Cobalt and nickel (minor constituent) were determined by ignition of a sample wrapped in filter paper and covered with oxalic acid. The mixture of oxides was dissolved in hydrochloric acid, electrodeposited as cobalt plus nickel from ammoniacal solution, and weighed as the metals. The oxide mixture was also ignited under hydrogen and weighed as the metals. Nickel was separated from a hydrochloric acid solution of the metals by anion exchange, precipitated with dimethylglyoxime, and weighed.

*Silver cyclohexanebutyrate* (Standard Sample 1068). Silver was determined by direct ignition of a sample wrapped in filter paper and covered with oxalic acid. The oxide was ignited under

hydrogen and weighed as the metal. Determinations were also made by dissolving the ignited oxide in nitric acid, precipitating with hydrochloric acid, and weighing the silver chloride.

*Sodium cyclohexanebutyrate* (Standard Sample 1069). Sodium was determined by direct ignition of a sample wrapped in filter paper and covered with oxalic acid. The residue was either converted into sodium sulfate and weighed after ignition at 900 °C or converted into sodium chloride and weighed after ignition at 600 °C.

*Calcium 2-ethylhexanoate* (Standard Sample 1074). Calcium was determined by direct ignition of a sample wrapped in filter paper and covered with oxalic acid. The residue was dissolved in hydrochloric acid, the calcium precipitated as calcium oxalate, and the calcium oxalate titrated with potassium permanganate solution.

### 3.7.4. Other Procedures

*Menthyl borate* (Standard Sample 1063). Boron was determined by bomb-fusing an 0.5-g sample with sodium peroxide and titrating the resulting boric acid with standard sodium hydroxide after the addition of mannitol.

*Mercuric cyclohexanebutyrate* (Standard Sample 1064). Mercury was determined in a sample by titration with ammonium thiocyanate, after extraction of organic matter with chloroform. Determinations were also made by extracting a sample with chloroform, precipitating the mercury with hydrogen sulfide, drying the precipitate at 110 °C, and weighing as mercuric sulfide.

## 3.8. Weight-stability of Standard Compounds

Preliminary studies showed that some of the compounds chosen as standards are fairly hygroscopic. Furthermore, drying by gentle heating (e.g., to 60 °C) at atmospheric pressure or in a vacuum oven was, in some instances, deleterious. Consequently, in order to ascertain the time for maximum absorption of moisture by each compound and the rate of drying after maximum absorption, the following procedure was employed.

A specimen (approximately 1 g) of the standard sample was transferred from the bottle to a weighing bottle (ground-glass stopper) and accurately weighed. The stopper was then removed and the material was exposed to an atmosphere of approximately 75 percent humidity in a closed desiccator containing a dish of saturated, aqueous sodium chloride solution. After the elapse of various periods of time, the stopper was replaced in the weighing bottle and the weight was determined. When equilibrium had been reached, the sample was dried in a desiccator containing phosphorus pentaoxide until the weight was constant. Most of the determinations were made in duplicate.

In addition, a 1-g specimen of each standard sample, as received by the analyst, was dried to constant weight over phosphorus pentaoxide in a desiccator. The percent loss in weight is given in column 4 of table 9.



TABLE 9. Loss in weight on drying, gain in weight at 75 percent humidity, and loss in weight on drying humidified material, for the standard samples

Serial No.	NBS Standard Sample No.	Original material <sup>a</sup>					Humidified material <sup>b</sup>		
		Dried over P <sub>2</sub> O <sub>5</sub>		In 75% humidity			Dried over P <sub>2</sub> O <sub>5</sub>		
		Time to equil	Loss in wt at equil	Time to equil	Gain in wt <sup>c</sup>		Time <sup>d</sup> to equil	Loss in weight <sup>e</sup>	
					in 7 hr	at equil		in 7 hr	at equil <sup>e</sup>
		hr	%	hr	%	%	hr	%	%
1-----	1050	24	1.0	2	0.08	0.08	2	1.0	1.0
2-----	1051	24	1.3	2	1.1	1.1	24	2.1	2.5
	1051a	24	0.9	2	1.9	1.9	24	2.2	2.8
3-----	1053	48	5.7	7	1.6	1.6	48	1.6	7.2
4-----	1054	48	0.1	7	0.06	0.06	48	0.09	0.2
5-----	1055	24	1.0	24	.06	.1	24	0.08	1.1
	1055a	48	1.2	48	.8	1.1	48	1.5	2.5
6-----	1056	2	0.01	2	.01	0.01	2	0.02	0.02
	1056a	2	.02	2	.03	.02	2	.06	.05
7-----	1058	24	.6	2	.2	.2	24	.7	.8
8-----	1059	24	.4	2	.2	.2	48	.9	1.2
	1059a	2	.02	16	.4	.6	2	.03	0.01
9-----	1060	24	.5	168	.3	2.8	24	2.5	3.5
	1060a	7	.4	168	.3	2.3	24	1.8	3.0
10-----	1061	216	2.6	336	<sup>f</sup> 1.5	<sup>g</sup> 2.2	48	2.0	2.8
	1061a	48	0.3	336	4.6	<sup>h</sup> 2.2	48	1.4	1.6
11-----	1062	144	1.9	24	0.8	1.2	48	0.8	2.9
	1062a	24	0.5	72	2.5	2.7	72	1.1	3.3
12-----	1064	2	.01	2	0.04	0.04	2	0.03	0.03
13-----	1065	72	.7	168	.4	.9	48	1.0	1.7
	1065a	24	.5	48	1.5	1.9	48	1.2	2.2
14-----	1067	24	4.9	<sup>h</sup> 48	-----	<sup>h</sup> 30.0	<sup>h</sup> 430	10.4	<sup>h</sup> 23.5
15-----	1068	48	0.5	24	0.4	0.6	24	1.7	2.0
16-----	1069	2	.01	168	2.3	28.0	48	8.1	28.0
	1069a	2	.01	168	2.2	28.0	48	8.4	28.0
17-----	1070	48	.8	2	0.2	0.2	24	0.9	0.9
	1070a	24	.5	2	.9	.9	24	1.0	1.2
18-----	1073	-----	-----	48	1.4	1.8	24	1.7	3.6
	1073a	2	.05	24	5.0	6.9	48	1.7	7.2
19-----	1063	2	.01	48	0.04	0.2	2	0.01	0.01
	1063a	2	.01	24	.04	.1	2	.06	.04
20-----	1072	48	.4	2	.4	.4	48	.8	1.0
21-----	1071	2	.01	2	.01	.01	2	.01	0.01
	1071a	2	.01	2	.02	.01	2	.01	.01
22-----	1066	2	.0	2	.0	.0	0	.0	.0
23-----	1057	2	.01	2	.01	.01	2	.01	.01
	1057a	2	.01	2	.04	.04	2	.02	.01
24-----	1052a	2	.02	2	.01	.02	2	.02	.02
25-----	1074	48	.4	48	5.1	5.6	48	2.9	4.5
26-----	1075	48	.5	24	0.1	0.1	48	0.5	0.7
27-----	1076	2	.01	24	.1	.2	2	.2	.2
28-----	1077	2	.01	24	.4	.5	2	.5	.5

<sup>a</sup> As received by analyst.  
<sup>b</sup> Kept in 75% humidity to equilibrium.  
<sup>c</sup> Calculated on the weight of original material taken.  
<sup>d</sup> Recommended drying time.  
<sup>e</sup> The figure in this column should be approximately equal to the sum of the figures in columns 4 and 7, unless hydrolysis occurred during the humidification.

<sup>f</sup> Gain of 3.5% after 48 hr.  
<sup>g</sup> This compound initially gained weight and then lost some of this gain in weight, at 75% humidity.  
<sup>h</sup> Equilibrium not reached. This compound should not be exposed to moisture.

The percent gain in weight, at equilibrium in 75-percent humidity, of a 1-g specimen of each standard sample (as received by the analyst) is given in column 7 of table 9. The percent loss in weight of this humidified material, on drying to constant weight over phosphorus pentaoxide in a desiccator, is given in column 10 of table 9. The figure in column 10 should be approximately equal to the sum of the figures in columns 4 and 7, unless hydrolysis occurred during the humidification. Standard Samples 1059a, 1061 and 1061a, 1067, and 1074 exhibit this behavior. From table 9, it may be seen that the weight-stabilities vary widely. It was concluded that, as a precautionary measure, bottles containing standard samples should be stored, tightly closed,

in desiccators containing phosphorus pentaoxide, and that, before use, the required amount of a compound should be dried over phosphorus pentaoxide for the length of time recommended in column 8 of table 9.

3.9. Dissolution in Petroleum Oils

In estimating the oil-solubility of the metallo-organic and other compounds, benzene, toluene, xylene, mineral spirits, mineral oil, white paraffin oil, and base oils (which were supplied by several oil companies) were used. One or more of the following attempts at dissolving the compounds were made.  
(1) Dissolving directly in oil, without heat or other solvents.

(2) Dissolving in oil, with moderate heating (below 100 °C).

(3) Dissolving in benzene, toluene, xylene, or mineral spirits, and diluting with the base oil.

(4) Dissolving in a solubilizing agent (such as a free carboxylic acid, a diketone, or an ester) and diluting with the base oil.

Early in the project, it was found that very few of the compounds could be dissolved by *method 1*. A slightly larger number of compounds could be dissolved by *method 2*, but the solutions usually redeposited material at room temperature. *Method 3* gave solutions that were more stable. *Method 4* gave the most stable and the most concentrated solutions of a given element.

These solubility tests were used both for evaluating the solubility of each compound and for comparing the solubilities of a variety of compounds of one element. The solubility of a compound was considered to be "satisfactory" if, by method 4, a solution could be prepared that had a concentration (of the element in question) of 500 ppm. In the subsequent discussion, the term "calculated weight" of a compound refers to *the weight of it which will provide 50 mg of the element of interest per 100 g of the final solution*. The solution was regarded as "stable" if it remained clear and devoid of visible change during several weeks at room temperature.

In the course of the work, a solution was developed which acts as both a solubilizer and a stabilizer of compounds dissolved in oil. This "solubilizing solution A" consists of a mixture of equimolar proportions of bis(2-ethylhexyl)amine and bis(2-ethylhexyl)dithiocarbamic acid in an equal volume of xylene.

### 3.9.1. Metal 2-Ethylhexanoates

Crude salts of 2-ethylhexanoic acid dissolved readily in benzene or xylene, and these solutions could be diluted with base oils to give stable solutions.

The purified, solid 2-ethylhexanoates of barium, calcium, copper, lead, lithium, and sodium gave stable solutions (metal concentration, 500 ppm) by dissolving the calculated weight in 3 to 6 ml of 2-ethylhexanoic acid and diluting to 100 g with lubricating oil.

Silver 2-ethylhexanoate gave a solution (silver concentration, 500 ppm) by first dissolving in 2-ethylhexylamine and then diluting to 100 g with base oil.

The iron (III) salt was dissolved by use of 6-methyl-2,4-heptanedione and 2-ethylhexanoic acid before addition of the oil.

The chromium salt underwent changes similar to those shown by chromium erucate and, after storage, could not be dissolved.

The solid salts of nickel and cobalt were practically insoluble in all solvents tested (with base oil).

### 3.9.2. Metal Erucates

Erucates of the metals of interest were found to be insoluble in the common organic solvents. Solutions having (a) the desired concentration of metal and (b) satisfactory stability were prepared by dissolving the calculated weight of the given salt in 3 to 6 ml of hot naphthenic acid (or hot 2-ethylhexanoic acid) and diluting to 100 g with lubricating oil.

Because of the high molecular weights of the metal erucates, a relatively large sample of each salt was needed in order to provide a final concentration (of metal) of 500 ppm; consequently, concentrations of 200 ppm were tested instead.

Stable solutions of the erucates of barium, lead, lithium, magnesium, potassium, sodium, strontium, and zinc, respectively, at a concentration of 200 ppm of the metal, were obtained by use of 4 to 6 ml of 2-ethylhexanoic acid as the solubilizing agent.

Silver erucate was dissolved in lubricating oil by use of solubilizing solution A.

By use of naphthenic acid or 2-ethylhexanoic acid, *freshly prepared* chromium erucate dissolved in base oils, but after the dry salt had been kept at room temperature for several days, it could no longer be dissolved.

### 3.9.3. Metal Dialkylthiocarbamates

The calculated weight of each compound dissolved readily in 3 to 5 ml of benzene, toluene, xylene, or mineral spirits at room temperature or, in a few instances, on heating; the solution was then diluted to 100 ml with lubricating oil, and the flask was stoppered. The solution was kept at room temperature for many weeks and was periodically observed for deposition of a precipitate or formation of a gel.

The following observations were made on dibutylthiocarbamates: the cadmium and cobalt compounds formed gels in base oils; the iron (III) compound had low solubility; but the copper, lead, nickel, and zinc compounds were satisfactory.

As could be anticipated, highly purified samples of the metal dithiocarbamates were less soluble in oil, and showed a greater tendency to crystallize from solution, than less pure samples. However, by dissolving the calculated weight of the dithiocarbamate (of copper, lead, nickel, and zinc) in 4 to 6 ml of solubilizing solution A and then adding sufficient lubricating oil to bring the weight to 100 g, each compound remained dissolved and the stability of the solution, on keeping, was satisfactory in all cases but one. (After a solution of lead dibutylthiocarbamate had been kept at room temperature for several weeks, a precipitate was formed which could not be redissolved in organic solvents.) Nickel bis(2-ethylhexyl)dithiocarbamate gave solutions that were stable for many months.



#### 3.9.4. Metal Chelates of Azomethines

The copper, nickel, and vanadium chelates of *N*-salicylidene(2-ethylhexyl)amine were soluble in lubricating oil. However, the oil solution of the vanadium chelate was not sufficiently stable, unless used on the same day that the solution was prepared; but addition of 4 to 6 ml of solubilizer A (per 100 g of final oil-solution) gave the desired stability.

#### 3.9.5. Metal Chelates of Diketones and Hydroxy Ketones

The metal chelates of the diketones having low molecular weight are soluble in benzene or xylene, and less soluble in mineral spirits, but their solubility in lubricating oils is very low.

The 2,4-pentanedione chelates of chromium, cobalt, copper, and iron are practically insoluble in oil, and solutions of the compounds in oil gave crystalline precipitates on being kept overnight at room temperature.

The 6-methyl-2,4-heptanedione chelates of aluminum and chromium were only obtained as oils, which were, however, very soluble in lubricating oil without addition of any solubilizer. The chromium, cobalt, iron, lead, and vanadium chelates of 1-phenyl-1,3-butanedione and 1,3-diphenyl-1,3-propanedione were also tested for oil-solubility. The chromium and iron chelates of 1-phenyl-1,3-butanedione were too low in solubility (by method 4), but the cobalt, lead, and vanadium chelates had satisfactory oil-solubility by method 4. The stability of this solution of this vanadium chelate in oil was satisfactory.

For the vanadium chelate of 1-phenyl-1,3-butanedione, a stable solution (metal concentration, 500 ppm) was prepared by dissolving the calculated weight in a hot solution of 3 ml of bis(2-ethylhexyl)amine and 3 ml of 6-methyl-2,4-heptanedione in 3 ml of xylene, adding 1 ml of 2-ethylhexanoic acid and 80 to 90 ml of lubricating oil, cooling to room temperature, and diluting to 100 g with lubricating oil. Although this vanadium compound is less oil-soluble than bis(*N*-salicylidene-2-ethylhexylamino)oxovanadium (IV), it is superior to the latter as regards (a) stability to light and air and (b) the stability of its solutions.

An oil solution of the chromium chelate of 2'-hydroxyacetophenone, at a metal concentration of 500 ppm, was prepared by heating the calculated weight with a mixture of 3 ml of 2-ethylhexanoic acid and 3 ml of 6-methyl-2,4-heptanedione until a clear solution formed and then diluting to 100 g with lubricating oil.

#### 3.9.6. Metal Cyclohexanebutyrates

The solid cyclohexanebutyrates of 19 metals were tested for solubility. The salts of cadmium, cobalt, copper, iron, lead, manganese, mercury, nickel, and zinc dissolve readily in chloroform but are less soluble in benzene or xylene.

With the exception of the chromium salt, all of the cyclohexanebutyrates studied were, by use of a solubilizer, dissolved in lubricating oil to afford stable solutions. For the salts of barium, calcium, lead, lithium, magnesium, manganese, mercury, nickel, potassium, sodium, and zinc, the calculated weight was dissolved in 4 to 6 ml of 2-ethylhexanoic acid, and the solution was diluted to 100 g with lubricating oil to afford a stable solution.

For the salts of cadmium, cobalt, copper, and silver, the calculated weight was dissolved in 4 to 6 ml of 2-ethylhexylamine, and the solution was diluted with oil.

For the salts of aluminum and iron, the calculated weight was dissolved in a hot mixture of 2-ethylhexanoic acid and 6-methyl-2,4-heptanedione, and the solution was diluted with oil.

Chromium cyclohexanebutyrate was unsatisfactory both as regards its physical state and its low solubility in oil (with all solubilizers tested).

#### 3.9.7. Miscellaneous Compounds

For the elements boron, phosphorus, and tin, the compounds that (of those tested) had the highest solubility in oil were menthyl borate, triphenyl phosphate, and dibutyltin bis(2-ethylhexanoate), respectively. Each dissolved in hot lubricating oil, at a concentration (of the element of interest) of 500 ppm, to give a stable solution. However, in routine work, it was found more practical to dissolve the calculated weight of each compound in 5 ml of hot xylene and dilute to 100 g with lubricating oil.

For silicon, the only solid derivative studied was octaphenylcyclotetrasiloxane, and this is practically insoluble in oils at room temperature. However, certain of the petroleum laboratories cooperating in testing the oil-solubility of the compounds discovered that this silicon compound gives a solution (silicon concentration, 200 ppm) which can be used satisfactorily if prepared as described in section 3.9.8.

Preparation of a stable, oil solution of the selected chromium compound has already been described (see section 3.9.5).

#### 3.9.8. Preparation of an Oil Solution Containing One Element of Interest, at the Desired Concentration

The required weight of the standard sample and the volume of each solvent needed, except that of the lubricating oil, are given in table 10. The procedure is exemplified by that for aluminum cyclohexanebutyrate (Standard Sample 1050).

Transfer approximately 1.0 g of this compound from the bottle to a small beaker and dry over fresh phosphorus pentaoxide in a desiccator for two hours. (Tightly close the bottle containing the remainder of the compound.) Quickly and accurately transfer 0.725 g of this dried salt to a weighed 200-ml flask. (This weight of salt is equivalent to 50 mg of aluminum.) Add 3 ml of xylene and 4 ml of 2-ethylhexanoic acid and heat the flask on a hot plate, with swirling and without charring, until a clear gel forms. Add 3 ml of 6-methyl-2,4-heptanedione and



TABLE 10. Preparation of a solution of one Standard Sample, in lubricating oil, at a concentration (of the element of interest) of 500 ppm <sup>a</sup>

Standard Sample					Solubilizers added			
Serial No.	NBS No.	Element of interest <sup>b</sup>	Approximate weight taken for drying	Weight of dried material taken	Xylene	2-Ethylhexanoic acid	6-Methyl-2,4-heptanedione	2-Ethylhexylamine
			g	g	ml	ml	ml	ml
1	1050	Al	1.0	0.725	3	4	3	-----
2	1051	Ba	0.2	.178	3	5	-----	-----
3	1053	Cd	.3	.209	2	<sup>c</sup> 2	-----	4
4	1054	Ca	.5	.476	3	5	-----	-----
5	1055	Co	.3	.292	2	<sup>c</sup> 2	-----	4
6	1056	Cu	.5	.313	2	<sup>c</sup> 2	-----	4
7	1058	Fe	.3	.259	3	4	3	-----
8	1059	Pb	.2	.133	3	5	-----	-----
9	1060	Li	1.5	1.25	3	5	-----	-----
10	1061	Mg	1.0	0.725	3	5	-----	-----
11	1062	Mn	0.5	.360	3	5	-----	-----
12	1064	Hg	.2	.138	3	5	-----	-----
13	1065	Ni	.3	.284	3	5	-----	-----
14	1067	K	.3	.263	3	5	-----	-----
15	1068	Ag	.2	.129	2	<sup>c</sup> 2	-----	4
16	1069	Na	.5	.417	3	5	-----	-----
17	1070	Sr	.3	.252	3	5	-----	-----
18	1073	Zn	.3	.270	3	5	-----	-----
19	1063	B	2.5	2.203	5	-----	-----	-----
20	1072	Cr	0.5	0.472	3	3	-----	-----
21	1071	P	.6	.526	5	-----	-----	-----
22	<sup>d</sup> 1066	Si	.2	<sup>e</sup> .142	4g	-----	-----	-----
23	1057	Sn	.3	.212	5	-----	-----	-----
24	1052	V	.4	.383	3	<sup>e</sup> 1	<sup>f</sup> 3	-----
25	1074	Ca	.5	.373	3	5	-----	-----
26	1075	Al	.8	.666	3	4	3	-----
27	1076	K	.6	.495	3	5	-----	-----
28	1077	Ag	.2	.118	2	<sup>c</sup> 2	-----	4

<sup>a</sup> Except for compound 22 (Standard Sample 1066).

<sup>b</sup> Wt of element, 50 mg, except for compound 22 (20 mg).

<sup>c</sup> Added just before addition of the lubricating oil.

<sup>d</sup> See separate description of procedure.

<sup>e</sup> Contains 20 mg of Si and gives a final concentration of 200 ppm.

<sup>f</sup> Plus 3 ml of bis-(2-ethylhexyl)amine.

continue heating and swirling until the gel disappears and a clear solution forms. To the hot solution, add 80 to 90 ml of lubricating oil, and gently shake the flask to mix the contents. Allow the flask to cool to room temperature and add enough lubricating oil to bring the total weight of the contents of the flask to  $100 \pm 0.5$  g. Stopper the flask and shake gently to insure a homogeneous solution. The concentration of aluminum in this solution is 500 ppm.

Because of its low solubility, a special procedure is necessary in order to prepare an oil solution of octaphenylcyclotetrasiloxane (Standard Sample 1066).

Accurately transfer 0.142 g of this compound to a weighed 200-ml flask. (This weight of compound is equivalent to 20 mg of silicon.) Add 4 g of xylene and heat the flask on a hot plate, with swirling and without charring, until the solid dissolves. In a separate flask, heat 95 g of lubricating oil to 75 °C, and carefully pour this hot oil into the silicon-containing solution. Allow the solution to cool to room temperature and add enough cool lubricating oil to bring the total weight of the contents of the flask to  $100 \pm 0.5$  g. Reheat the flask immediately to 75 °C under a reflux condenser and keep the solution under the condenser, at this temperature, during use. The concentration of silicon in this solution is 200 ppm.

### 3.9.9. Preparation of an Oil Solution Containing Several Elements of Interest, at the Desired Concentration

Stable solutions of a mixture of the compounds, containing each element of interest at the desired concentration, can be prepared.

Of the 24 compounds selected as standards, the aluminum, chromium, iron, and vanadium compounds require (a) the most heating and (b) the presence of at least two solubilizers (in xylene) for dissolution in the oil. Consequently, one (or

more) of these compounds was dissolved first. Moreover, the compounds of silver and mercury are sensitive to prolonged heating and, so, they should be added last. For the other compounds, the order of addition is immaterial.

An appropriate solubilizer, or mixture thereof, is chosen, and the calculated weight of one of the compounds is added; this compound is dissolved completely. The other compounds are now added, one at a time, each being dissolved completely before the next one is added. As a rule, the more compounds added, the greater the solubility in the mixture. Finally, the cooled solution is diluted to 100 g with lubricating oil.

The volume of solubilizer needed depends on the particular mixture of compounds to be dissolved, but in no instance exceeded 12 ml per 100 g of final oil-solution.

The following is a precise description of the preparation of a blend containing nine elements of interest, each at a concentration of 250 ppm.

The solubilizing agent was prepared by placing 5 ml of 2-ethylhexanoic acid, 4 ml of 6-methyl-2,4-heptanedione, and 2 ml of xylene in a weighed, 200-ml Erlenmeyer flask. The calculated weight of aluminum cyclohexanebutyrate (see table 11) was weighed into a small beaker and carefully transferred to the flask (without permitting the salt to touch the inside of the flask and without creation of dust of the compound). The suspension was gently heated on a hot plate, with swirling, until the salt had dissolved to a clear solution. Using a clean spatula each time, and



TABLE 11. Order of addition and weights of compounds used for preparation of a blended solution of nine elements in oil

Element	Compound	Wt of compound <sup>a</sup> used <sup>b</sup>
		g
Al	Aluminum cyclohexanebutyrate.....	0.363
Cr	Tris (2'-hydroxyacetophenono) chromium (III).....	.236
V	Bis (1-phenyl-1,3-butanediono) oxovanadium (IV).....	.193
Ba	Barium cyclohexanebutyrate.....	.089
Fe	Iron cyclohexanebutyrate.....	.130
Cu	Cupric cyclohexanebutyrate.....	.157
Co	Cobalt cyclohexanebutyrate.....	.146
Mg	Magnesium cyclohexanebutyrate.....	.363
Ni	Nickel cyclohexanebutyrate.....	.142

<sup>a</sup> Equivalent to 25 mg of the particular element.

<sup>b</sup> Per 100 g of final solution, to give a concentration (of the element) of 250 ppm.

with precautions to avoid contamination from transfer of traces of one compound to a container of another compound, the calculated weight of each of the other compounds was added, one at a time (in the order given in table 11), and completely dissolved before the next compound was added. After each addition, the mixture was gently heated, tilted, and rotated in order to wash down any particles adhering to the inside of the flask.

After the last compound had been added and dissolved, 2 ml of bis(2-ethylhexyl)amine was added. The hot solution in the flask was now poured into the small beaker, and back and forth, until all traces of solid in the beaker had dissolved. After returning the solution to the flask, the beaker was washed with six 15-ml portions of lubricating oil, and these rinsings were all transferred to the flask. The oil solution was now allowed to cool to room temperature, and cool lubricating oil was added to the flask until the weight of the solution was  $100 \pm 0.5$  g. The solution was reheated to 85 °C, allowed to cool to room temperature, transferred to a bottle, and tightly stoppered.

A precise determination of the maximum concentration attainable for each element of interest, either individually in oil plus solubilizers, or as a mixture of the standard compounds in oil plus solubilizers, has not been made. However, solutions having concentrations *much higher* than those given have been prepared and found to be stable. All solutions prepared from the standard compounds (according to the directions given) have, up to this time, shown no signs of deterioration on keeping.

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<sup>8</sup> Deceased, May 22, 1961.





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