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DEVELOPMENT OF COMPOSITE SPECTROPHOTOMETRIC PROCEDURES
FOR THE ANALYSIS OF LOW-ALLOY STEELS
AND OF ALUMINUM AND ITS ALLOYS

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THE UNIVERSITY OF TEXAS

NOVEMBER 1952

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**DEVELOPMENT OF COMPOSITE SPECTROPHOTOMETRIC PROCEDURES
FOR THE ANALYSIS OF LOW-ALLOY STEELS
AND OF ALUMINUM AND ITS ALLOYS**

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November 1952

*Materials Laboratory
Contract No. AF 33(038)-23168
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**Wright Air Development Center
Air Research and Development Command
United States Air Force
Wright-Patterson Air Force Base, Ohio**

FOREWORD

This is the final report of work performed under the terms of Contract No. AF 33(038)-23168 between Wright Air Development Center, Wright-Patterson Air Force Base, Ohio, and The University of Texas, Austin, Texas. The work was initiated under Research and Development Order No. 616-11, "Procedures for Compositional Analysis of Aircraft Alloys", and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Mr. O. O. Srp acting as project engineer. The period of operation of the contract began on 1 June 1951, to run for one year. By Modification No. M1(52-161) the time of performance was extended to 31 July 1952 for completion of the experimental work and delivery of the final report to the Government, and to 30 September 1952 for compliance with all other provisions of the contract.

The project was under the direction of Gilbert H. Ayres, with Stanley H. Simonsen as associate director. H. F. Young served as group leader for the experimental work, in which the following shared: M. H. Booth, J. H. Braun, Jean Gray, J. W. Ho, W. A. Jones, C. M. Maddin, K. B. McCollum, and Mary Meyer.

ABSTRACT

Procedures have been developed for the spectrophotometric analysis of the constituents of low-alloy steels and of aluminum and its alloys, using a single sample to give a composite solution in which most of the elements are determined. In general, the conventional spectrophotometric methods for the various elements have been employed, modified as necessary for the use of the single composite solution technique. The methods have been tested thoroughly, in the hands of several different operators, by applying them to a variety of standard samples; the results of these tests are tabulated in the report.

Detailed procedures, with explanatory notes, to serve as a practical laboratory manual are given for the spectrophotometric analysis of low-alloy steels for chromium, copper, manganese, molybdenum, nickel, phosphorus, silicon, and vanadium, and for the analysis of aluminum and its alloys for chromium, copper, iron, manganese, molybdenum, nickel, titanium, and vanadium. The molybdisilicic acid method for silicon in the aluminum samples did not give satisfactory results; the conventional gravimetric method for this determination is recommended.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDING GENERAL:

/S/ M.R. Whitmore

for M. E. SORTE
Colonel, USAF
Chief, Materials Laboratory
Directorate of Research

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SECTION I

SPECTROPHOTOMETRIC METHODS INVESTIGATED

The objective of this research was to develop composite schemes for the spectrophotometric analysis of low-alloy steels for chromium, copper, manganese, molybdenum, nickel, phosphorus, silicon, and vanadium, and for the spectrophotometric analysis of aluminum and its alloys for chromium, copper, iron, manganese, molybdenum (up to 1%), nickel, silicon, titanium (up to 2%), and vanadium (up to 1%). After a literature survey, existing methods were tested for suitability to the problem at hand, and modifications applied where indicated. The methods were checked by running several replicate determinations on synthetic samples, National Bureau of Standards standard samples, and samples furnished by the contracting agency.

Various methods investigated for the different constituents are summarized briefly below. The composite methods for low-alloy steels are outlined, and analytical results tabulated, in Section II; similar information for aluminum and its alloys is given in Section III. Section IV gives the composition of the standard samples used. In Section V some general considerations concerning spectrophotometric methods are discussed. Sections VI and VII constitute a working laboratory manual for the completed schemes of analysis.

CHROMIUM

1. Hematoxylin as the color-developing reagent proved unsatisfactory on account of the long time (more than two hours) required for development of the red color.

2. The diphenylcarbazide method for chromium was impractical due to rapid fading of the purple color; the reaction was also critically sensitive to pH.

3. In the method adopted for subsequent use, the chromium was oxidized with perchloric acid to dichromate and the transmittancy measured against a part of the solution which had been reduced with a ferrous solution. Sensitivity and reproducibility were improved by high concentration of ferric ion, provided by addition, to the sample solution, of sufficient iron solution to give a constant amount of total iron. Slight modifications of procedure were required, depending upon whether the chromium content was low (up to 0.1%) or high (above 0.1%).

COPPER

1. Although copper can be determined by measurement of the blue cupric ammonia complex, the reaction is not very sensitive and is subject to interference from many other cations which form either insoluble hydroxides or colored complexes with ammonia.

2. Alpha-benzoinoxime, added to an alkaline solution of the sample containing tartrate, provided a means of separation of copper by extraction of

the copper benzoinoximate into chloroform. The yellow-green color of the chloroform extract was suitable for photometric measurement. Of the elements present in low-alloy steels and in aluminum alloys, only nickel above 2% and cobalt above 0.25% interfered by giving low results for copper.

IRON

Iron was determined by means of the red color produced by treating iron(II) solutions with ortho-phenanthroline in the presence of an acetate buffer. In the analysis of aluminum alloys, granulated lead was added to separate any copper (iron was simultaneously reduced); complete reduction of the iron was effected by addition of hydroxylamine hydrochloride, and the buffered solution was color-developed with ortho-phenanthroline.

MANGANESE

Manganese was satisfactorily determined by oxidation of the sample solution with potassium periodate in phosphoric acid solution, and measurement of the resulting permanganate color.

MOLYBDENUM

1. Phenylhydrazine hydrochloride, added to an acetic acid solution of molybdenum(VI), produces a red color which is suitable for spectrophotometric measurement. In samples containing more than about 5% molybdenum, iron(III) did not interfere, and vanadium did not interfere unless present in larger amount than molybdenum. In samples containing less than 5% molybdenum, iron(III) interfered, although interference could be eliminated by selective reduction to iron(II). For samples containing small amounts of molybdenum the thiocyanate method was preferred.

2. The sample was taken into solution under oxidizing conditions; if chromium was present in significant amounts it was removed by volatilization as chromyl chloride. After adding sodium thiocyanate and stannous chloride, the mixture was extracted with amyl acetate, and the extract (orange to red) was used for color measurement against a blank which had been carried through all steps of the procedure. In samples containing very small amounts of molybdenum, a large excess of stannous chloride was required to insure complete reduction of iron(III) so that it would not interfere by formation of the red ferric thiocyanate complex.

NICKEL

Nickel was satisfactorily determined on the basis of the red color produced by ammoniacal dimethylglyoxime after oxidation to nickel(IV) with iodine in sulfuric-phosphoric acid solution containing ammonium citrate. Iodine was found to be a more satisfactory oxidizing agent than bromine; addition of the oxidizing agent prior to addition of dimethylglyoxime prevented the precipitation of nickel(II) dimethylglyoximate. Aluminum samples containing copper required removal of the copper by sulfide precipitation from acid solution prior to the determination of nickel.

PHOSPHORUS

Steel samples were dissolved, and fumed down with perchloric acid to insure complete oxidation of phosphorus to phosphate. Iron(III) was reduced by addition of sodium sulfite solution. A mixture of ammonium molybdate, hydrazine sulfate, and sodium sulfite was added, and the blue color developed by heating in a boiling water bath. Careful attention to procedural details was required.

SILICON

1. The silicomolybdic acid method was applied by adding, to the sample solution, ammonium molybdate solution and sulfuric acid, followed after a few minutes by stannous chloride to reduce the complex to molybdenum blue. The color reaction was somewhat sensitive to the concentrations of reagents; iron must be removed prior to the determination; only small amounts of phosphorus could be tolerated, and then only if the acidity was carefully adjusted.

2. Silicate solutions containing hydrochloric acid were treated with ammonium molybdate and with oxalic acid (to prevent interference from phosphate), and extracted repeatedly with amyl alcohol--ethyl acetate mixture. Upon addition of stannous chloride to the extract, a blue color developed which was photometered against a similarly-prepared blank. Although interference from phosphate could be eliminated by the use of sufficient oxalic acid, fading of the blue color was so rapid as to render the method impractical.

3. By following the procedure described in 2 above, through the extraction but without the addition of stannous chloride, a yellow extract of silicomolybdic acid was obtained. Interference from iron(III) was negligible. The color appeared to be quite stable, but the method was not well reproducible.

4. By the use of sodium fluoride, interference from both iron(III) and phosphorus was prevented in the determination of silicon through the silicomolybdate color. Steel samples were dissolved in nitric acid and oxidized with potassium persulfate. An aliquot of the diluted solution was treated with sodium molybdate solution, allowed to stand for ten minutes, then treated with sodium fluoride solution; to another aliquot, used for the blank, the reagents were added in reverse order, with the intervening time interval. Sample and blank were contained in plastic absorption cells for transmittancy measurements. Application of this method to the determination of silicon in aluminum alloys has not given satisfactory results.

TITANIUM

1. Chromotropic acid (sodium-1,8-dihydroxynaphthalene-3,6-disulfonate) produces a yellow color with titanium(IV) suitable for spectrophotometric estimation. Interference from the higher oxidation states of vanadium and molybdenum was eliminated by their reduction with sulfur dioxide prior to addition of the color-developing reagent. Maximum color development occurred in a solution of pH 1.5; color intensity was found to be critically sensitive to pH.

2. Hydrogen peroxide produces a yellow to orange color with titanium-(IV) solutions that served for the determination of titanium. The peroxidized sample was measured against a portion of the sample to which no hydrogen peroxide was added. Vanadium, and to a less extent molybdenum, interfere by also giving colors upon peroxidation, although the absorption maxima of the various colors occur at somewhat different wave lengths. The simultaneous determination of titanium, vanadium, and molybdenum, by measurement of optical densities at three different wave lengths and simultaneous solution of three equations, gave only fair results for titanium and molybdenum, with large discrepancies appearing in the amount of vanadium found. For aluminum alloys containing both titanium and vanadium, a separation of these components should be made. Titanium was separated by precipitation with phenylarsonic acid; the precipitate was decomposed with nitric and sulfuric acids, and the color developed with hydrogen peroxide.

VANADIUM

1. The yellow color of phosphotungstovanadic acid was found to be suitable for the determination of vanadium when present alone, but was subject to interference from iron, chromium, cobalt and copper; also, the wave length of maximum absorption was found to be somewhat dependent upon the amount of vanadium present and the amount of phosphoric acid added.

2. The red color produced by treatment of vanadate solutions with ortho-phenylenediamine in the presence of phosphoric acid (to complex the iron) required one to two hours for complete development at room temperature, and about 15 minutes at temperatures near the boiling point. The only common alloying element which interfered was chromium(VI), and its interference was eliminated by reduction to chromium(III) with sodium nitrite solution. Good replication of results was not obtained.

3. Various other color reactions were investigated. The blue color obtained when vanadate solutions were reduced with iron(II) was not of sufficient intensity to be useful for small amounts of vanadium. Aniline and its derivatives gave blue colors which progressively darkened to black; other oxidizing agents such as chromium(VI) gave similar colors. Vanadate solutions, reduced by zinc, sulfur dioxide, or iron(II) salts in the presence of phosphate, gave a red-violet color; molybdenum(VI) and tungsten(VI) interfered by giving intense blue colors on reduction. N-Phenylanthranilic acid in sulfuric acid solution gave a purple color with vanadate; other oxidizing agents in the solution interfered by giving a similar color reaction.

4. Hydrogen peroxide, which produces a yellow color in acid solutions of vanadate, was found to be the most satisfactory reagent for the determination of vanadium. Titanium(IV) and chromium(VI) interfere seriously, and must be removed. Satisfactory results in the analysis of vanadium were obtained by precipitation as lead vanadate, using tungstate as a carrier, followed by dissolution of the precipitate in perchloric acid and determination with hydrogen peroxide. Although alpha-benzoinoxime in acid solution precipitates vanadium(V), there are indications that the precipitation is not complete; chromium(VI) is also precipitated, but its interference in the peroxide method for vanadium can be eliminated by addition of sodium nitrite solution. Results for vanadium after separation with alpha-benzoinoxime were

about 5% low. By the dissolution procedure used for aluminum samples (described later), vanadium divides between the alkali-soluble portion and the alkali-insoluble portion; hence a separate sample must be dissolved in hydrochloric acid for use in the vanadium determination. Titanium was precipitated with phenylarsonic acid; from the filtrate, chromium was removed by volatilization as chromyl chloride by treating with sodium chloride and fuming down with perchloric acid; in the residual solution, vanadium was then determined by the hydrogen peroxide method.

SECTION II

RESULTS OF ANALYSIS OF LOW-ALLOY STEELS

The methods were applied to National Bureau of Standards standard samples (identified as NBS with the sample number), and to samples furnished by the contracting agency, Air Research and Development Command (ARDC). As many different determinations as possible were made on a single solution basis. Several replicate aliquots of each sample solution were analyzed. Samples were selected to give a wide range of composition with respect to the desired constituents. Results are summarized by giving, for each sample number, the range and the average of the constituent found, and the average deviation; for comparison, the certificate value and range of results are also given. The composition of the samples used is tabulated in Section IV.

2.1. DISSOLUTION OF SAMPLE

An exact ten gram sample of steel was dissolved in nitric acid, added in small portions. In a few cases a very small amount of residue (carbon) remained, which was not filtered off; it settled rapidly when the solution was subsequently diluted. The solution was made up volumetrically to 250 ml. and mixed thoroughly. Each milliliter of the final solution contained 0.0400 gram of the original sample. Suitable aliquots of this solution were used for spectrophotometric analysis, as described in the following paragraphs.

2.2. DETERMINATION OF CHROMIUM

For low chromium steels (up to 0.1%), a 25 ml. aliquot of the sample solution was fumed down with perchloric acid to oxidize the chromium to dichromate; after making up the cooled solution to known volume (e.g., 50 ml.), a portion of the solution was reduced by iron(II) solution, to serve as a blank against

Table 1

NBS Sample	% Chromium Found		Avge. Devn.	% Chromium Certif.	
	Range	Average		Range	Average
12e	0.049-0.050	0.050	0	0.047-0.054	0.050
19e		0.037	0	0.037-0.040	0.038
22c	0.006-0.007	0.006	0	0.006-0.010	0.007
72d	0.99 -1.00	1.00	0	1.02 -1.03	1.03
PB-20662#	0.49 -0.50	0.50	0.005		0.56

#Sample furnished by ARDC.

which a portion of the unreduced solution was measured. From the measured transmittancy, the chromium content was determined by reference to a calibration curve prepared from NBS standard sample 111b. For steels containing more than 0.1% chromium, a proportionally smaller aliquot was taken, and ferrous perchlorate solution added to give a total of one gram of iron; the mixture was then oxidized with perchloric acid and chromium determined as outlined above. Results are shown in Table 1.

2.3. DETERMINATION OF COPPER

Method 1

A suitable aliquot of the composite solution was treated with Rochelle salt (sodium potassium tartrate), and sodium hydroxide solution added to adjust the pH within the range 11.3 to 12.3. After adding alpha-benzoinoxime the mixture was extracted with chloroform. The chloroform layer was separated, and a second extraction made with a smaller volume of chloroform. The chloroform extracts were diluted with chloroform to known volume, and the transmittancy measured against a blank prepared by carrying the reagents through all steps of the procedure. The calibration curve was prepared from data obtained by following the above procedure with NBS standard sample 19e. The results are shown in Table 2.

Table 2

<u>NBS</u> <u>Sample</u>	<u>% Copper</u> <u>Range</u>	<u>Found</u> <u>Average</u>	<u>Avge.</u> <u>Devn.</u>	<u>% Copper</u> <u>Range</u>	<u>Certif.</u> <u>Average</u>
22c	0.010-0.012	0.010	0	0.009-0.014	0.011
10e	0.030-0.032	0.031	0.001	0.029-0.235	0.032
72d	0.035-0.041	0.039	0.002	0.039-0.046	0.041
30d	0.088-0.091	0.090	0.001	0.085-0.107	0.092
153	0.099-0.102	0.101	0.001	0.090-0.11	0.099
12e	0.132-0.145	0.139	0.003	0.137-0.148	0.142

Method 2

This method was the same as Method 1, except that a single extraction with an accurately measured volume of chloroform was made, and the extract used directly for the transmittancy measurement. The results, shown in Table 3, were calculated from a calibration made by the use of NBS standard sample 12e.

Table 3

<u>NBS Sample</u>	<u>% Copper Range</u>	<u>Found Average</u>	<u>Avge. Devn.</u>	<u>% Copper Range</u>	<u>Certif. Average</u>
22c	0.007-0.013	0.011	0.002	0.009-0.014	0.011
10e	0.027-0.032	0.030	0.002	0.029-0.035	0.032
30d	0.096-0.100	0.098	0.002	0.085-0.107	0.092
19e	0.178-0.182	0.180	0.002	0.160-0.174	0.166

2.4. DETERMINATION OF MANGANESE

A suitable aliquot of the sample solution was heated with potassium periodate and phosphoric acid, to oxidize the manganese to permanganate, and the cooled solution diluted to known volume. A portion of the solution was reduced with sodium nitrite solution for use as a blank, against which the transmittancy measurements were made. NBS standard sample 100a was used for standardizing the method. Results are summarized in Table 4.

Table 4

<u>NBS Sample</u>	<u>% Manganese Range</u>	<u>Found Average</u>	<u>Avge. Devn.</u>	<u>% Manganese Range</u>	<u>Certif. Average</u>
19e	0.487-0.500	0.493	0.007	0.482-0.498	0.491
72d	0.525-0.537	0.531	0.003	0.533-0.540	0.537
10e		0.650	0	0.631-0.636	0.634
12e	0.721-0.742	0.726	0.008	0.70 -0.711	0.706
22c	0.750-0.756	0.753	0.003	0.740-0.756	0.746
30d		0.800	0	0.78 -0.793	0.786
PB 20662 [#]	0.535-0.540	0.538	0.002	0.53 -0.55	0.54

[#]Sample furnished by ARDC.

2.5. DETERMINATION OF MOLYBDENUM

An aliquot of the sample solution was treated with sodium thiocyanate and tin(II) chloride solutions, and the reduced molybdenum thiocyanate was extracted into amyl acetate. Transmittancy measurements of the extract were made against a blank carried through the procedure. (The amount of chromium encountered in low-alloy steels did not interfere; in high chromium steels, chromium should be removed, by volatilization as chromyl chloride, prior to reduction and color development.) NBS Chromium-Molybdenum Steel, standard sample 72d, was used for calibration of the method. Results are shown in Table 5.

Table 5

NBS Sample	% Molybdenum Found		Avge. Devn.	% Molybdenum Certif.	
	Range	Average		Range	Average
19e	0.013-0.014	0.013	0	One anal.	0.012
12e		0.018	0	0.014-0.018	0.016
30d	0.033-0.034	0.033	0	0.029-0.036	0.034
72d [#]	0.208-0.212	0.210	0.002	0.205-0.212	0.210

[#]Separate sample from that used in establishing calibration.

2.6. DETERMINATION OF NICKEL

A suitable aliquot of the sample solution was treated with sulfuric-phosphoric acid mixture and ammonium citrate, then oxidized by the addition of iodine; the color was developed by addition of ammoniacal solution of dimethylglyoxime. The blank, against which transmittancy readings were taken, was prepared by carrying a portion of the sample solution through all steps of the procedure, except that dilute ammonium hydroxide was substituted for the dimethylglyoxime solution. NBS Nickel Steel, standard sample 33c, was used for the calibration. Results are summarized in Table 6.

Table 6

NBS Sample	% Nickel Found		Avge. Devn.	% Nickel Certif.	
	Range	Average		Range	Average
10e	0.016-0.018	0.017	0.001	0.018-0.021	0.020
12e	0.053-0.057	0.055	0.001	0.055-0.061	0.058
19e	0.090-0.093	0.091	0.001	0.083-0.102	0.093
72d	0.127-0.129	0.128	0.001	0.123-0.128	0.125
30d	0.151-0.152	0.151	0	0.144-0.158	0.150

2.7. DETERMINATION OF PHOSPHORUS

A portion of the sample solution was fumed down with perchloric acid, and the iron(III) was reduced by addition of sodium sulfite. The color was developed by addition of a solution containing ammonium molybdate, hydrazine sulfate and sodium sulfite. The blank solution was prepared by treating a portion of the sample solution in the same way, except that the molybdate reagent was omitted. The calibration curve for the determination was established by the use of a standard solution of potassium dihydrogen phosphate. Representative results are shown in Table 7.

Table 7

<u>NBS Sample</u>	<u>% Phosphorus Found Range</u>	<u>Average</u>	<u>Avge. Devn.</u>	<u>% Phosphorus Certif. Range</u>	<u>Average</u>
12e	0.010-0.012	0.011	0.001	0.013-0.016	0.014
72d	0.014-0.017	0.016	0.001	0.015-0.018	0.017
19e	0.027-0.035	0.031	0.005	0.031-0.035	0.033
10e	0.078-0.079	0.079	0	0.081-0.085	0.083
22c	0.075-0.085	0.080	0.005	0.081-0.085	0.083

2.8. DETERMINATION OF VANADIUM

The aliquot of sample solution was made 7 molar in hydrochloric acid and extracted with isopropyl ether to remove the iron. The aqueous layer was evaporated to fuming with perchloric acid, sodium chloride was added, and heating continued to volatilize chromyl chloride. After making the solution to known volume, hydrogen peroxide was added to develop the color. Transmittancy measurements were made against a portion of the final solution which had not been peroxidized. The calibration curve was established by the use of a standard solution of ammonium vanadate. Typical results are shown in Table 8.

Table 8

<u>NBS Sample</u>	<u>% Vanadium Found Range</u>	<u>Average</u>	<u>Avge. Devn.</u>	<u>% Vanadium Certif. Range</u>	<u>Average</u>
19e	0.007-0.009	0.008	0.001	One anal.	0.009
30d	0.180-0.194	0.186	0.005	0.184-0.193	0.190

2.9. DETERMINATION OF SILICON

Although satisfactory reproducibility could not be obtained by the use of aliquots of the composite solution, good precision was attained when separate small samples were used for the silicon determination. Half-gram samples were dissolved in nitric acid, with the addition of potassium persulfate, and made up to known volume. An aliquot of the solution was treated with sodium molybdate, and after a ten-minute interval sodium fluoride was added; the blank, against which transmittancy measurements were made, was prepared by adding the developing reagents in reverse order, with the ten-minute interval. Experimental points for the calibration curve were obtained by the use of mixtures of various NBS standard samples to give the desired silicon concentrations. Results are shown in Table 9.

Table 9

<u>NBS Sample</u>	<u>% Silicon Range</u>	<u>Found Average</u>	<u>Avge. Devn.</u>	<u>% Silicon Certif. Range</u>	<u>Average</u>
129a	0.025-0.028	0.027	0.001	0.018-0.024	0.021
10e	0.065-0.070	0.067	0.002	0.065-0.073	0.067
22c		0.105	0	0.096-0.101	0.098
19e	0.170-0.173	0.172	0.001	0.163-0.179	0.173
100a	0.240-0.242	0.241	0.001	0.241-0.248	0.243
12e	0.274-0.278	0.277	0.001	0.271-0.283	0.278
30d	0.291-0.295	0.293	0.001	0.282-0.295	0.286
21d	0.330-0.331	0.330	0	0.324-0.338	0.332

SECTION III

RESULTS OF ANALYSIS OF ALUMINUM ALLOYS

The methods were applied to National Bureau of Standards (NBS) standard samples, and to samples furnished by the contracting agency (ARDC). Several replicate aliquots of each sample were analyzed. The samples contained wide ranges of composition with respect to the desired constituents. Results are summarized by giving, for each sample number, the range and the average of the constituent found, and the average deviation. For comparison, the per cent of the constituent given is included in the tabulations; in the cases of the NBS standard samples, this is the certified value; in the cases of the ARDC samples, the given value is the average of closely agreeing duplicates obtained by a commercial testing laboratory by conventional chemical methods. In the tabulated results, National Bureau of Standards standard samples of aluminum are designated by the prefix NBS; all other aluminum samples were furnished by the contracting agency. The composition of the samples used is tabulated in Section IV. Detailed procedures for the analysis are given in Section VII.

3.1. DISSOLUTION OF SAMPLE

In the usual method for dissolving aluminum alloys in preparation for analysis, the alloy is attacked first with concentrated sodium hydroxide solution, and the alkali-insoluble residue then dissolved in acid (hydrochloric, nitric, sulfuric, etc., or mixtures of certain of these acids.) However, in the conventional methods for copper and nickel, the residue insoluble in alkali is filtered off and dissolved separately in acid. For the determination of several minor constituents in the solution from a single sample, a rather large sample (e.g., ten grams) must be taken. Successive use of strong sodium hydroxide followed by acid, in such a case, involves the formation of such a large amount of aluminum salts and sodium salts that difficulties arise from the crystallization of these salts from the solution. Therefore, it is advantageous to effect a separation after the alkali attack; the alkaline solution contains all of the aluminum. The residue is then dissolved in acid and used for analysis of most of the minor constituents. Vanadium divides between the alkali-soluble and alkali-insoluble portions, and is best analyzed by the use of a separate small sample dissolved in hydrochloric acid.

An exact ten gram sample of the aluminum alloy was treated with 20% sodium hydroxide solution, added in small portions, and the mixture finally boiled until reaction ceased. The cooled mixture was transferred quantitatively to a centrifuge bottle and the residue settled by centrifugation. The supernatant solution was removed, and the residue washed several times with water. (The solution and washings contain the aluminum, any zinc which is present, and part of the vanadium.) The residue was treated with nitric acid and boiled until no black residue remained. In some samples, a dense white precipitate remained at this point; it was dissolved by the addition of perchloric acid. Any finely-divided flocculent precipitate (silicic acid) was removed by filtration using a fine porosity filter. The solution was transferred quantitatively to a 250 ml. volumetric flask and made up to volume. Each ml. of this solution was equivalent to 0.0400 g. of the original sample. Aliquot portions of this solution were used for the analyses given below, unless otherwise noted.

3.2. DETERMINATION OF CHROMIUM

To a suitable aliquot of the sample solution, sufficient ferrous perchlorate solution was added to give a total of one gram of iron. The mixture was fumed down with perchloric acid to oxidize the chromium to dichromate, and the chromium determined as in the analysis of chromium in steel, Section 2.2, using the same calibration curve. Results are shown in Table 10.

Table 10

<u>Sample</u>	<u>% Chromium Found Range</u>	<u>Average</u>	<u>Avge. Devn.</u>	<u>% Chromium Given Range</u>	<u>Average</u>
NBS 85a	0.228-0.242	0.237	0.004	0.226-0.24	0.231
WW-T-783		0.01	0		0.05
WW-T-787		0.20	0	0.21 -0.22	0.22
AN-A-11	0.21 -0.22	0.22	0.005		0.26
78S	0.20 -0.21	0.21	0.003	0.22 -0.23	0.22
ML-9006	2.53 -2.65	2.56	0.04	2.65 -2.67	2.66

3.3. DETERMINATION OF COPPER

Most of the aluminum alloys analyzed were rather high in copper content, in which case an aliquot of the sample solution was diluted volumetrically (e.g., 1:10 or 1:50), and an aliquot of the diluted solution used for the

Table 11

<u>Sample</u>	<u>% Copper Found Range</u>	<u>Average</u>	<u>Avge. Devn.</u>	<u>% Copper Given Range</u>	<u>Average</u>
NBS 85a	2.44 -2.47	2.46	0.01	2.46-2.49	2.48
NBS 86c	7.83 -8.05	7.94	0.05	7.88-7.96	7.92
WW-T-787		0.011	0		0.01
ML-9006	0.352-0.364	0.36	0.005	0.36-0.37	0.36
ML-9060	3.49 -3.86	3.60	0.18	3.65-3.70	3.68
WW-T-783	4.38 -4.43	4.40	0.03	4.41-4.43	4.42

analysis. The copper was determined in the chloroform extract from an alkaline tartrate solution containing alpha-benzoinoxime, as in the analysis of copper in steel, Section 2.3, using the same calibration curve. Typical results are given in Table 11.

3.4. DETERMINATION OF IRON

The color reaction of iron(II) with ortho-phenanthroline is so sensitive that the iron concentration of the test sample must be very small. For samples relatively high in iron, an aliquot of the sample solution was diluted volumetrically, and a suitable aliquot of the diluted solution taken for the analysis. Copper in the solution was removed by the addition of granulated lead; the precipitated copper and excess lead were removed by filtration. The iron in the solution was reduced by addition of hydroxylamine hydrochloride, the solution buffered with acetic acid--sodium acetate mixture, and the color was developed by adding ortho-phenanthroline. The blank, against which transmittancy was measured, consisted of a portion of the sample solution to which all reagents except ortho-phenanthroline were added. The calibration curve was prepared from a standard iron solution made by dissolving pure iron wire in perchloric acid. Results are shown in Table 12.

Table 12

<u>Sample</u>	<u>% Iron Range</u>	<u>Found Average</u>	<u>Ave. Devn.</u>	<u>% Iron Range</u>	<u>Found Average</u>
NBS 604		0.42	0		0.45
NBS 601	0.52 -0.55	0.53	0.01		0.52
NBS 85a		0.209	0	0.20-0.213	0.208
NBS 86c		0.89	0	0.89-0.92	0.90
WW-T-787	0.162-0.164	0.163	0.001		0.20
MN-9060		0.235	0	0.25-0.26	0.26
AN-A-11	0.254-0.258	0.256	0.002	0.26-0.27	0.26
WW-T-783		0.279	0	0.30-0.31	0.30

3.5. DETERMINATION OF MANGANESE

Suitable aliquots of the sample solution were oxidized with potassium periodate in phosphoric acid solution, and the manganese (as permanganate) determined as in the analysis of manganese in steel, Section 2.4, using the same calibration curve. Table 13 gives typical results.

Table 13

<u>Sample</u>	<u>% Manganese Found Range</u>	<u>Average</u>	<u>Avge. Devn.</u>	<u>% Manganese Given Range</u>	<u>Average</u>
NBS 86c	0.038-0.043	0.041	0.003	0.037-0.05	0.041
NBS 85a	0.66 -0.67	0.66	0.005	0.65 -0.67	0.66
AN-A-11	0.10 -0.12	0.11	0.01	0.013-0.015	0.014 [#]
ML-9060	0.300-0.312	0.306	0.006	0.30 -0.31	0.30
WW-T-783	0.68 -0.69	0.68	0.005	0.69 -0.70	0.70
ML-9006	3.25 -3.30	3.28	0.02	3.29 -3.31	3.30

[#]See Note below.

Note: The "nominal composition" given by ARDC for manganese in sample AN-A-11 is "0.05 - 0.15". The values submitted by ARDC to the director of this project for duplicate analyses by a commercial laboratory were "0.013 and 0.015%." Our findings on this sample are within the range of the nominal composition, and indicate either a decimal point error by the commercial laboratory or a typographical error in submitting the analysis report.

3.6. DETERMINATION OF MOLYBDENUM

No aluminum samples containing molybdenum were available for test. The method was simulated by preparing a solution of NBS aluminum alloy standard sample 85a in nitric and perchloric acids, and a standard solution of ammonium molybdate; the solutions were mixed in various proportions, and the molybdenum determined by reduction with tin(II) chloride, treatment with sodium thiocyanate and extraction into amyl acetate, as in the determination of molybdenum in steel, Section 2.5. The results, shown in Table 14, are calculated to per cent molybdenum based on the weight of aluminum alloy represented.

Table 14

<u>% Molybdenum Taken</u>	<u>% Molybdenum Found</u>
0.020	0.020
0.12	0.12
0.36	0.35
0.72	0.74
1.00	1.04

Because no aluminum samples containing molybdenum were available for test, it was not possible to determine the behavior of molybdenum in the dissolution process. Although molybdenum itself is insoluble in strong sodium hydroxide, there is no certainty of its similar behavior in alloys involving possible intermetallic compounds. Until the behavior of aluminum-molybdenum alloys toward sodium hydroxide is established, use of the acidic solution of the alkali-insoluble portion of the alloy for molybdenum analysis is of doubtful value. It would probably be better to determine molybdenum in a solution made by direct acid attack on a separate sample of the alloy.

3.7. DETERMINATION OF NICKEL

Unless the nickel content is quite high, copper interferes with the determination, and must be removed. The aliquot of the sample solution taken for nickel analysis should contain from 0.05 to 0.30 mg. of nickel; copper was precipitated by the addition of a small amount of sodium sulfide solution to the acidic sample solution. The precipitated copper sulfide was filtered off, washed, and the filtrate and washings boiled to expel hydrogen sulfide. The solution was made up to known volume, and the nickel determined as in the method for nickel in steel, Section 2.6, using the same calibration curve. Results are shown in Table 15.

Table 15

<u>Sample</u>	<u>% Nickel Range</u>	<u>Found Average</u>	<u>Avg. Devn.</u>	<u>% Nickel Range</u>	<u>Given Average</u>
NBS 86c	0.028-0.030	0.029	0.001	0.02 -0.035	0.030
NBS 85a	0.406-0.413	0.410	0.003	0.40 -0.42	0.41
NBS 604	1.95 -1.98	1.96	0.01		2.00

3.8. DETERMINATION OF TITANIUM

Sulfuric acid was added to a suitable aliquot of the sample solution and the mixture evaporated to small volume. After cooling, the solution was made up to known volume. To a portion of the solution hydrogen peroxide was added to develop the color, and transmittancy measurement made against another portion of the unperoxidized solution used as a blank. The calibration curve was prepared from data obtained by the use of a standard solution of titanium made by dissolving titanium dioxide in sulfuric acid. Results for the determination of titanium are shown in Table 16. Vanadium in the sample solution in more than trace amounts interferes; in this case a separation of titanium from vanadium was made as described in Section 3.9. In addition to Sample ML-9006, the determination of titanium after separation with phenylarsonic acid was tested with a synthetic aluminum sample to which titanium was added; the results were calculated to the basis of per cent titanium in the aluminum.

Table 16

<u>Sample</u>	<u>% Titanium Found Range</u>	<u>Average</u>	<u>Avge. Devn.</u>	<u>% Titanium Given Range</u>	<u>Average</u>
NBS 85a	0.013-0.015	0.013	0	0.014-0.02	0.016
NBS 86c		0.034	0	0.033-0.036	0.035
NBS 601		0.016	0		0.015
NBS 604		0.101	0		0.100
WW-T-783		0.01			0.03
AN-A-11		0.02			0.03
ML-9006 [#]	0.64-0.66	0.65	0.01	0.63-0.65	0.64
Synthetic [#]		0.26			0.25

[#]Titanium separated by precipitation with phenylarsonic acid.

3.9. DETERMINATION OF VANADIUM

In the procedure for the dissolution of the aluminum alloy for preparation of the composite sample (Section 3.1), vanadium divides between the alkali-soluble and the alkali-insoluble portions. For this reason, vanadium analysis was made on a separate small sample (e.g., 0.5 to 1 g.) of the alloy which was dissolved in dilute hydrochloric acid, then oxidized by hot concentrated nitric acid. In the absence of titanium, vanadium was determined directly in the solution by the same method as its determination in steel, Section 2.8. When titanium was present, it interfered extensively with the vanadium determination; separation of titanium from vanadium was therefore required. The sample solution containing the titanium and vanadium, acidified with nitric acid, was treated with phenylarsonic acid solution to complete precipitation of titanium phenylarsonate. The precipitate was filtered off and washed.

1. The titanium phenylarsonate precipitate was heated with nitric and sulfuric acids to destroy the organic matter, and the titanium determined with hydrogen peroxide as in Section 3.8; see Table 16.

2. The filtrate and washings were diluted to known volume, and the vanadium was determined by hydrogen peroxide, as in Section 2.8. Table 17 shows the results of vanadium determination in sample ML-9006, and also in NBS cast aluminum standard sample 86c to which a known amount of vanadium was added.

Table 17

<u>Sample</u>	<u>% Vanadium Found</u> <u>Range</u>	<u>Average</u>	<u>Avge.</u> <u>Devn.</u>	<u>% Vanadium Given</u> <u>Range</u>	<u>Average</u>
ML-9006 [#]	0.84-0.86	0.85	0.01	0.89-0.91	0.90
Synthetic [#]		0.52			0.50

[#]Vanadium determination after separation of titanium.

3.10. DETERMINATION OF SILICON

Attempts to determine silicon in aluminum samples spectrophotometrically by means of the molybdisilicate method of Aluminum Research Institute, as well as by various other methods in the recent literature, were unsuccessful. Many modifications of different methods were tried, but all gave widely divergent results. It should be remarked that considerable controversy exists in the literature on the validity of results of various spectrophotometric methods for silicon in aluminum samples. Because concordant results for silicon could not be obtained spectrophotometrically, silicon was determined gravimetrically.

The aluminum sample was dissolved in sodium hydroxide solution, and the solution evaporated to small volume. Perchloric acid and a small amount of nitric acid were added, and the mixture evaporated to dense fumes to dehydrate the silica. After dilution, the silica was filtered off and washed with 1% sulfuric acid; the filter paper containing the silica was ignited in a platinum crucible, and weighed. Hydrofluoric acid and sulfuric acid were added, the mixture was evaporated to dryness and then ignited, and the residue weighed. The loss in weight represented silicon as silicon dioxide. Results are shown in Table 18.

Table 18

<u>Sample</u>	<u>% Silicon Found</u> <u>Range</u>	<u>Average</u>	<u>Avge.</u> <u>Devn.</u>	<u>% Silicon Given</u> <u>Range</u>	<u>Average</u>
NBS 86c	0.70-0.71	0.71	0.003	0.67-0.69	0.68
NBS 85a	0.09-0.14	0.11	0.02	0.108-0.12	0.114

SECTION IV

COMPOSITION OF STANDARD SAMPLES USED

The methods of analysis investigated in this project, and proposed for use in routine work, were checked by applying them to samples of known composition. The composition of National Bureau of Standards standard samples of steel is shown in Table 19. Table 20 gives the composition of aluminum samples obtained from National Bureau of Standards, as well as those furnished by the contracting agency; for the latter samples the values given are averages of duplicate results obtained by a commercial testing laboratory by conventional chemical methods.

National Bureau of Standards samples serve as convenient and reliable standards for calibration purposes; in general, a sample of relatively high content of the particular element was used for calibration for the determination of that element.

Table 19

NATIONAL BUREAU OF STANDARDS STEEL SAMPLES

No.	<u>Mn</u>	<u>P</u>	<u>Si</u>	<u>Cu</u>	<u>Ni</u>	<u>Cr</u>	<u>V</u>	<u>Mo</u>
10e	0.634	0.083	0.067	0.032	0.020	0.023	0.004	0.010
12e	0.706	0.014	0.278	0.142	0.058	0.050	0.002	0.016
19e	0.491	0.033	0.173	0.166	0.093	0.038	0.009	0.012
21d	1.03	0.041	0.332	0.107	0.190	0.100	0.005	0.035
22c	0.746	0.083	0.098	0.011	0.004	0.007	0.006	0.001
30d	0.786	0.031	0.286	0.092	0.150	1.15	0.190	0.034
32d	0.795	0.012	0.301	0.096	1.19	0.710	0.003	0.038
33c	0.733	0.017	0.233	0.031	3.23	0.052	0.002	0.032
34a	0.501	0.023	0.276	0.222	0.232	0.275	0.007	0.003
55c	0.016	0.003	0.001	0.040	0.016	0.003	0.001	0.004
72d	0.537	0.017	0.276	0.041	0.125	1.03	0.005	0.210
100a	1.66	0.020	0.243	0.050	0.032	0.051	0.003	0.008
111b	0.71	0.012	0.30	0.028	1.81	0.071	0.002	0.256
129a	0.806	0.094	0.021	0.021	0.027	0.021	0.004	0.007
153	0.219	0.025	0.187	0.099	0.107	4.14	2.04	8.39
PB-20662#	0.54	0.010	0.17		1.75	0.56		0.26

#Sample furnished by contracting agency (ARDC).

Table 20

ALUMINUM SAMPLES

National Bureau of Standards samples are designated by prefix NBS; all other samples were furnished by the contracting agency (ARDC).

<u>No.</u>	<u>Cu</u>	<u>Mg</u>	<u>Mn</u>	<u>Ni</u>	<u>Cr</u>	<u>Fe</u>	<u>Si</u>	<u>Zn</u>	<u>Ti</u>	<u>V</u>
NBS 85a	2.48	1.58	0.66	0.41	0.231	0.208	0.114	0.019	0.016	0.001
NBS 86c	7.92	0.002	0.041	0.030	0.029	0.90	0.68	1.50	0.035	
NBS 601	4.38	0.39	0.81		0.020	0.52	0.88		0.015	
NBS 604	3.98	1.56		2.00		0.45	0.27	0.029	0.100	
78S	1.78	2.70			0.22		0.07	6.50		
ML-9060	3.68	2.63	0.30	1.85		0.26				
AN-A-11	1.50	2.54	0.014 [#]		0.26	0.26	0.14	5.33	0.03	
WW-T-787	0.01	2.45			0.22	0.20	0.10			
WW-T-783	4.42	1.52	0.70	0.01	0.05	0.30	0.16	0.17	0.03	
ML-9006	0.36		3.30		2.66	1.32	1.00		0.64	0.90

[#]See note on page 15 regarding this value.

SECTION V

SPECTROPHOTOMETRIC METHODS OF ANALYSIS

General Considerations

The methods described below were designed for use with a Beckman Spectrophotometer Model DU equipped with matched 1.00-cm. absorption cells. Cells made of Corex glass are satisfactory for measurements at wavelengths down to 330 millimicrons. The methods given are for operation of the instrument with a tungsten light source, and for measurements at wavelengths in the visible range; methods involving measurement in the ultraviolet were not proposed because their application for routine use would require a hydrogen discharge lamp which has rather limited operating life, and the use of silica absorption cells of high replacement cost. For measurement of solutions in volatile solvents, such as chloroform or amyl acetate, glass-stoppered absorption cells are recommended. High-quality absorption cells can be obtained at nominal cost from Pyrocell Manufacturing Company, 207 E. 84th Street, New York 28, N. Y.

For the details of operation of the Beckman Spectrophotometer, the analyst is referred to the instruction manual furnished by the manufacturer of the instrument. It is recommended that the instrument be operated at constant high sensitivity, by using the sensitivity control knob backed off three turns from its clockwise limit. From time to time the focus of the instrument should be checked as described in the manufacturer's bulletin of operating instructions. It is advisable also to check the accuracy of the wavelength scale; this is easily accomplished by the use of a solution of potassium permanganate (preferably a standard solution) stabilized by the addition of phosphoric acid and potassium periodate. If the focus is in good adjustment, the instrument should give good resolution of rather sharp absorption bands at 526 and 546 millimicrons (transmittancies about 11% and 12%, respectively, for a permanganate solution containing 20 p.p.m. of manganese); and also indications of faint absorption bands at about 510 and 568 millimicrons (transmittancies about 20% and 30%, respectively, for a 20 p.p.m. manganese solution).

In all cases the transmittancy (or optical density) of the color-developed solution should be measured against a blank solution having a composition as near as possible to that of the sample, except for the desired light-absorbing species. In the usual case in analysis of steel or aluminum samples, one portion of the solution for test is processed with the reagents, including the color-developing reagent, and another portion is processed with the reagents except for the color-developing reagent. In this way, constituents, other than the one desired, which absorb slightly at the wavelength of the measurement are compensated by cancellation in the blank.

For each method the spectral characteristics of the system were evaluated by measuring the transmittancy, at frequent wavelength intervals, over a span of several hundred millimicrons. Except where otherwise noted, the wavelength specified for use in the analytical measurements is the wavelength at which maximum light absorption (highest optical density or lowest transmittancy) occurs.

The accuracy attainable in photometric analysis and the range over which reliable results can be attained have been discussed in a publication by Ayres. Additional considerations have appeared in publications by Hiskey and by Grigman. Briefly, it may be said that the most accurate results are obtained when

the transmittancy is about 37% (optical density 0.434), although the error is not much larger in the range of about 20% to 70% transmittancy (optical density about 0.700 to 0.155); the relative analysis error becomes very large at transmittancies below 10% and above 80%. Therefore, for best results the sample weight and/or the aliquot taken should be such as to give a solution having a transmittancy within the limits of about 20% to 70%, when measured against a corresponding blank solution. The ranges given for the determinations in the following sections are based upon these considerations, and upon the use of absorption cells of 1.00 cm. light path.

In general, each method should be calibrated by the use of a standard sample closely approximating the composition of the materials to be analyzed. For example, in the analysis of steels, the method for a given constituent is calibrated by the use of a National Bureau of Standards standard sample containing a relatively large amount of that constituent, either by the use of separately weighed samples of different sizes, or by the use of different aliquots of a single sample. If a suitable standard sample of sufficiently high content of the desired constituent is not available, it may be practical to use a sample of low content of desired constituent to which suitable increments of a standard solution of the desired constituent have been added. Calibration by the use of solutions of chemical compounds other than primary standards of known purity would require their assay by methods of recognized reliability. Whatever the method used, several calibration points should be established by the use of quantities of desired constituent to give a range of transmittancies from about 90% to 10%, and each calibration point should be based upon several closely agreeing replicates of the same concentration. It should be emphasized that different instruments even of the same manufacturer have somewhat different responses, hence each analytical laboratory should calibrate the method for the particular instrument used. Furthermore, the calibration should be checked from time to time.

A calibration curve provides the simplest means of converting photometric data to concentration of desired constituent. The logarithm of per cent transmittancy may be plotted (ordinate) against concentration (abscissa), or optical density may be plotted against concentration; in the former case, the use of semi-log graph paper is convenient because the ordinate is explicit in transmittancy and implicit in log transmittancy. In plotting the calibration curve, the concentration may be expressed in one of several ways: parts per million (p.p.m. = mg. per liter); mg. per ml. (or any other convenient volume); per cent of desired constituent when a sample and aliquot of specified size are taken and for measurement in solution of fixed volume; etc. The choice is one of convenience for the purpose at hand. If the system under measurement conforms to Beer's law, either method of plotting (log transmittancy, or optical density) results in a straight line, the former with a negative slope, and the latter with a positive slope. By the standard series method of operation, it is immaterial whether the system conforms to Beer's law or not, provided the same method is used for determination as for calibration. If the system conforms to Beer's law, the calibration curve (a straight line) can be established with relatively few experimental points; calibration graphs with considerable curvature (representing deviations from Beer's law) are the exception rather than the rule, but if met require a large number of calibration points. Calculation of concentrations from the extinction coefficient for the system should not be employed unless conformity to Beer's law has been established; in any case, such calculations are more laborious and are not recommended for routine work.

SECTION VI

PROCEDURE FOR ANALYSIS OF LOW-ALLOY STEELS

In the reagents listings in Sections VI and VII, acids listed only by name shall be understood to be the concentrated C.P. acid generally available for laboratory use; the same applies to ammonium hydroxide. Dilutions of these reagents are designated by volume ratio to water, the first figure being that of concentrated reagent; e.g., 1:3 nitric acid indicates one volume of concentrated nitric acid added to three volumes of water. In all cases, water used for dilution of reagents and samples means distilled water. All chemicals are to be of the best quality readily available, and in general should conform to A.C.S. specifications. Weight per cent solutions of solids are based upon grams of solid solute per 100 ml. of solution.

The customary techniques in the use of volumetric apparatus, such as volumetric flasks and pipets, are assumed.

Attention is called to the customary precautions in the handling and use of perchloric acid.

6.1. DISSOLUTION OF SAMPLE

Reagent

Nitric acid, 1:1.

Procedure

Weigh accurately a 10.00 g. sample of steel (Note 1). Place 150 ml. of 1:1 nitric acid in an 800 ml. beaker, add the steel sample in small portions (Note 2) and finally heat until dissolution of the sample is complete (Note 3). Cool the solution and transfer it quantitatively to a 250 ml. volumetric flask, washing well from beaker to flask. Dilute the solution to volume, and mix it thoroughly (Note 4).

Notes

1. The sample weight to be taken, and the final volumetric dilution of the sample solution, may be varied from the values given, depending upon the content of the elements to be determined (if this be approximately known in advance) and upon the number of replicate analyses to be made for each constituent by the use of aliquots of the composite solution. For the determination of constituents (e.g., vanadium) that are frequently found in low alloy steels only in very small amounts, it is probably advantageous to dissolve a separate sample and use the entire solution for the determination of the desired constituent without having to take large aliquots of a sample solution.

2. More rapid dissolution is effected by adding the sample to the acid, rather than vice versa. Care must be taken not to add too much sample at once, lest the reaction become too vigorous and the material froth over. A too rapid effervescence may be moderated by adding a little cold water.

3. Some samples may leave a small amount of residue (silica and carbon); the amount is usually so small as to be negligible on a ten gram sample. The residue should be removed by filtration through a fine-textured filter paper, receiving the filtrate directly in the volumetric flask.

4. Thorough mixing of a solution in a volumetric flask requires many inversions and much shaking. A better procedure is to pour the solution back and forth between initially dry beakers.

6.2. DETERMINATION OF CHROMIUM

The method is essentially that of Singer and Chambers, the chromium being determined as dichromate.

Reagents

Nitric acid, 1:1.

Perchloric acid.

Ferrous perchlorate solution: dissolve 325 g. of $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in water and dilute volumetrically to 500 ml. 1.0 ml. = 0.10 g. of iron.

Procedure

For chromium below 0.1%: Transfer a 25 ml. aliquot of the composite sample solution to a 500 ml. Erlenmeyer flask. Add 20 ml. of perchloric acid, heat to fumes of perchloric acid and continue the heating for 5 to 8 minutes after the body of the flask has cleared of acid fumes. Immediately quench the mixture (Note 1) by placing the flask in a pan of cold tap water. When the contents of the flask have solidified, cool the sides of the flask with running tap water, then add 10 ml. of distilled water to the flask. Transfer the solution quantitatively to a 50 ml. volumetric flask, and dilute to volume; mix thoroughly. Remove a portion of the solution, and add ferrous perchlorate solution dropwise until the orange color of the dichromate is completely discharged (Note 2); this solution serves as the blank. Transfer the blank and a portion of the unreduced solution to absorption cells, and measure the transmittancy at 330 millimicrons (Note 3). Determine the chromium content by reference to the calibration curve.

For chromium above 0.1%: Transfer a proportionally smaller aliquot (Note 4) of the sample solution to a 500 ml. Erlenmeyer flask, add the required volume of ferrous perchlorate solution to give a total of one gram of iron in the solution (Notes 3, 5), and proceed exactly as above.

Calibration

The method is best calibrated by the use of a standard steel containing chromium (such as NBS Chromium-Molybdenum Steel 72d, 1.03% chromium). Weigh out several samples of different size, and dissolve in 1:1 nitric acid. To each sample add sufficient ferrous perchlorate solution to give a total of one gram of iron in the solution (Note 5), and develop the color as described in the above procedure. Measure the transmittancies at 330 millimicrons, and plot the values by one of the methods suggested in Section V. (See Note 6.)

Range

The range suitable for accurate measurement is about 2 to 16 p.p.m. of chromium, corresponding to 0.1 to 0.8 mg. of chromium per 50 ml. of the solution measured.

Notes

1. Decomposition of hot perchloric acid gives some hydrogen peroxide, which reduces dichromate in hot solution; by quickly cooling the mixture, reduction of dichromate by hydrogen peroxide becomes so slow as to be of no consequence.

2. Only a few drops of ferrous perchlorate solution are required.

3. The wavelength at which minimum transmittancy occurs is somewhat dependent upon acid concentration; careful attention to the details of procedure is required.

4. For samples containing more than about 0.1% chromium, the transmittancy of the solution from a 25 ml. aliquot of composite solution is below the value at which good analysis accuracy is attained. The aliquot should be selected to get the final solution within the range indicated above.

5. The sensitivity of the method, as well as the wavelength at which minimum transmittancy occurs, is dependent upon the iron concentration. Accurate results require the same amount of iron to be present in all samples, in both calibration and analysis. The ferrous perchlorate solution, to be added when necessary, should be measured from a buret or a graduated pipet. Ferric chloride is not suitable for providing the required iron content; if it were added prior to fuming down with perchloric acid, chromium would be volatilized as chromyl chloride; if added after the fuming with perchloric acid, the color of ferric chloride would interfere with the measurement of the dichromate. If ferrous ammonium sulfate were used to provide the iron content, fuming down with perchloric acid may lead to the formation of difficultly soluble products. For these reasons ferrous perchlorate is used to provide the iron content. After fuming down with perchloric acid and diluting, iron(III) in the perchloric acid solution has only a pale lavender color.

6. As an alternative method of calibration, one gram samples of a low chromium steel, such as NBS 22c, can be dissolved and appropriate increments of standard potassium dichromate added to provide the chromium content; measurements are made as before.

6.3. DETERMINATION OF COPPER

The method is essentially that given by Dunleavy, Wiberley and Harley; it is based upon the color of copper benzoinoximate in a chloroform extract.

Reagents

Alpha-Benzoinoxime (Eastman No. 1377): 0.5% solution in 10% sodium hydroxide solution.

Chloroform.

Nitric acid, 1:2.

Sodium hydroxide, 10% aqueous solution.

Sodium potassium tartrate (Rochelle salt): 300 g. of $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ dissolved in 500 ml. of water.

Procedure

Transfer a suitable aliquot of the composite sample solution (Note 1) to a 250 ml. beaker, add 25 ml. of sodium potassium tartrate solution, and, while testing the solution with a pH meter, slowly add sodium hydroxide solution until the pH is within the limits 11.3 to 12.3 (Note 2). Add 2 ml. of alpha-benzoinoxime solution (Note 3), then transfer the solution quantitatively to a small separatory funnel. Add 30 ml. of chloroform, and shake the funnel vigorously for one to two minutes. Let the funnel stand until the liquid layers are well separated, then run off the chloroform (lower) layer containing the copper benzoinoximate through a small dry filter paper (Note 4) into a 50 ml. volumetric flask. Repeat the extraction with 10 ml. of chloroform as before, and add the chloroform solution to the main extract in the volumetric flask. Add chloroform to the mark, and mix the solution thoroughly. Prepare a blank (Note 5) by carrying the reagents through all steps of the procedure. Measure the transmittancy at 440 millimicrons, and determine the copper content of the sample by reference to the calibration curve. (See Note 6.)

Calibration

To calibrate the method, dissolve several different weights (Note 7) of a standard steel (such as USS sample 19e, 0.16% copper, or USS sample 19a, 0.14% copper) in 10 to 20 ml. of 1:2 nitric acid, and carry each sample through the procedure given above. Measure the transmittancy, against a similar blank, at 440 millimicrons, and construct the calibration curve.

Range

The range suitable for accurate measurement is about 2 to 16 p.p.m. of copper, corresponding to 0.1 to 0.3 mg. of copper per 50 ml. of the solution measured.

Notes

1. Aliquots of from 25 to 5 ml. of the composite sample solution are suitable for samples containing from about 0.02% to 0.1% copper. For samples of much higher copper content, a portion of the composite sample solution should be diluted volumetrically (for example, 1:10) and an aliquot of the diluted solution taken for analysis.

2. The extraction of copper into the final solution is quite dependent upon the pH of the solution from which extraction is made. In the pH range 11.3 to 12.3, the extraction is complete, but at pH values below and above these limits the amount of copper extracted decreases quite sharply.

3. A large excess of alpha-benzoinoxime reagent is to be avoided; if the sample contains more than about 0.25% nickel, a large excess of the reagent causes extraction of the nickel.

4. Filtration through a dry paper serves to take up minute drops of water which would render the chloroform solution turbid.

5. For preparation of the blank, start with a few milliliters of dilute nitric acid.

6. For a somewhat more rapid (but less accurate) procedure, a single extraction with 25 ml. (accurately measured) of chloroform may be used; in this case, the calibration should be established by the same procedure.

7. Instead of several samples of different weights, a single larger sample could be dissolved and made to known volume, from which different aliquots can be taken for the calibration points. In this case, however, any error in sample weight would not be detected; for this reason, the use of several samples of different weights is to be preferred.

6.4. DETERMINATION OF MANGANESE

The method originated by Willard and Greathouse is used; manganese in the solution is oxidized with periodate to permanganate which is photometered. The procedures are essentially as described by Lundell, Hoffman and Bright (pp. 198-200).

Reagents

Ammonium persulfate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$.
Nitric acid, 1:2.
Phosphoric acid.
Potassium nitrite, 2% aqueous solution.
Potassium periodate (meta), KIO_4 .

Procedure

Transfer a suitable aliquot of the sample solution (Note 1) to a 250 ml. beaker. Add 10 ml. of phosphoric acid and 0.3 g. of potassium periodate, and boil the mixture for about 5 minutes to oxidize the manganese to permanganate. Cool the solution, transfer it quantitatively to a volumetric flask (Note 2), dilute to volume with water, and mix thoroughly. To a small portion of the solution add potassium nitrite solution dropwise, until the purple color is discharged; this solution serves as the blank. Measure the transmittancy of the solution at 526 millimicrons, and calculate the manganese content of the sample by reference to the calibration curve.

Calibration

The method is calibrated by the use of a standard steel containing manganese (such as NBS Manganese Steel 100a, 1.66% manganese). Dissolve several weighed samples, of appropriately different weights, in dilute nitric acid with heating as necessary. If any dark residue (carbon) remains, add ammonium persulfate to the hot solution until a total of one gram has been used. Carry the samples through the above procedure, starting with the addition of phosphoric acid, finally bringing the solution to known volume. Measure the transmittancy at 526 millimicrons, and construct the calibration curve.

Range

The range suitable for accurate measurement is about 2 to 16 p.p.m. of manganese, corresponding to 0.2 to 1.6 mg. of manganese per 100 ml. of solution measured.

Notes

1. Aliquots of 25 to 5 ml. may be used, depending upon the manganese content of the sample and upon the volume of the final solution for measurement.

2. Volumes of 50, 100, or 250 ml. are convenient, depending on the amount of manganese in the aliquot taken.

6.5. DETERMINATION OF MOLYBDENUM

The method is based upon the amber to red color of reduced molybdenum thiocyanate which is extracted into amyl acetate. The procedure given below is essentially that given by the U. S. Steel chemists in "Sampling and Analysis of Carbon and Alloy Steels."

Reagents

Amyl acetate.

Hydrochloric acid.

Nitric acid.

Perchloric acid.

Sulfuric acid, 1:6.

Sodium chloride.

Sodium thiocyanate: 10% aqueous solution.

Stannous chloride solution: dissolve 300 g. of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 200 ml. of concentrated hydrochloric acid, and dilute to one liter.

Procedure

Transfer a suitable aliquot (Note 1) of the sample solution (Note 2) to a small separatory funnel, and add 25 ml. of 1:6 sulfuric acid. Add 5 ml. of sodium thiocyanate solution (Note 3) and 10 ml. of stannous chloride solution, with good mixing after each addition. Add 25 ml. (Note 4) of amyl acetate (Note 5), and shake the mixture vigorously for about 30 seconds. Add 10 ml. more sodium thiocyanate solution and 5 ml. more stannous chloride solution (Note 6), and again shake the mixture for about 30 seconds. Allow the funnel to stand until there is good separation of the liquid layers, then draw off and discard the lower aqueous layer. To the solution in the separatory funnel add 25 ml. of 1:6 sulfuric acid, 5 ml. of sodium thiocyanate solution, and 5 ml. of stannous chloride solution, shake the mixture well, allow the funnel to stand for good separation of layers, and draw off and discard the aqueous layer. Rinse the funnel stem by drawing off a small amount of the amyl acetate solution containing the molybdenum, then transfer some of the amyl acetate solution to an absorption cell. Simultaneously with the treatment of the sample, prepare a blank by starting with 25 ml. of 1:6 sulfuric acid and carrying it through all steps of the procedure. Measure the transmittancy of the solution at 468 millimicrons, and calculate the molybdenum content of the sample by reference to the calibration curve.

Calibration

Dissolve several samples of different weights (Note 7) of a standard steel containing molybdenum (such as NBS Chromium-Molybdenum Steel 72d, 0.210% molybdenum) in nitric acid, with the addition of some hydrochloric acid if necessary to hasten dissolution. Add 10 ml. of perchloric acid, and heat the mixture to fuming. To the hot solution add, in small increments, about 1 g. of sodium chloride, and continue the fuming until the red-brown chromyl chloride is completely expelled. Then cool the solution and treat the sample exactly as given in the above procedure. From the measured transmittancies at 468 millimicrons, construct the calibration curve.

Range

An appropriate working range is about 0.5 to 5 p.p.m. of molybdenum, corresponding to 0.0125 to 0.125 mg. of molybdenum in 25 ml. of the amyl acetate extract.

Notes

1. By the procedure described, 5 ml. of the composite sample solution is satisfactory for steels containing from about 0.006% to 0.06% molybdenum. For steels of higher molybdenum content, an aliquot of the sample solution may be volumetrically diluted (for example, 1:10) and an aliquot of the diluted solution used for color development.

2. For cases in which the chromium content is high, removal of chromium should be made. Treat an aliquot of the sample solution with 10 ml. of perchloric acid, and heat to strong fuming. To the hot solution add about 1 g. of sodium chloride, in small increments, and continue the fuming until the red-brown chromyl chloride is completely volatilized. Then cool the solution and proceed with the determination as described.

3. Solutions of potassium thiocyanate or ammonium thiocyanate would serve equally well, except following the removal of chromium, as in Note 2, with perchloric acid; potassium and ammonium perchlorates are insoluble, whereas sodium perchlorate is considerably more soluble.

4. Measure the amyl acetate accurately with pipet or buret.

5. Butyl acetate may be substituted for amyl acetate, although the latter is preferred on account of its lower solubility in water.

6. It is essential that sufficient stannous chloride be used to effect complete reduction of iron(III) to iron(II), otherwise the iron(III) will form the red ferric thiocyanate, which interferes with the color measurement.

7. Alternatively, a single large sample may be dissolved, the solution made up to known volume, and different aliquots processed for the several calibration points.

6.6. DETERMINATION OF NICKEL

The general method described by Cooper was used, with slight modifications. A quite similar procedure has been given by Mitchell and Mellon.

Reagents

Ammonium citrate solution: Dissolve 540 g. of the solid in water and dilute to one liter.

Ammonium hydroxide, 1:1.

Dimethylglyoxime, 0.1% ammoniacal solution: dissolve 1 g. of dimethylglyoxime in 500 ml. of concentrated ammonium hydroxide and dilute to one liter.

Iodine solution: dissolve 8 g. of potassium iodide and 2.6 g. of iodine in water and dilute to one liter.

Nitric acid.

Sulfuric-phosphoric acid mixture: to 850 ml. of water add 75 ml. of sulfuric acid and 75 ml. of phosphoric acid.

Procedure

Transfer a suitable aliquot (Notes 1, 2, 3) of the sample solution to a 50 ml. volumetric flask. Add the following reagents in the order given, with good mixing after each addition: 1 ml. of sulfuric-phosphoric acid mixture; 5 ml. of ammonium citrate solution (Note 4); 5 ml. of iodine solution (Note 5); 10 ml. of dimethylglyoxime solution (Note 6); water to dilute to volume. Simultaneously treat another identical aliquot with the same reagents, except use 10 ml. of 1:1 ammonium hydroxide instead of the dimethylglyoxime; this portion serves as the blank. Five to ten minutes (Note 7) after the addition of dimethylglyoxime, measure the transmittancy of the solution at 540 millimicrons (Note 8), and calculate the nickel content by reference to the calibration curve.

Calibration

The method is conveniently calibrated by use of a standard nickel steel (such as NBS Nickel Steel 33c, 3.28% nickel). Accurately weigh a sample of 0.2 to 0.4 g. (Note 9) of the standard steel. Add 25 ml. of the sulfuric-phosphoric acid mixture, and heat until reaction ceases; add nitric acid slowly and with good stirring, to oxidize the iron (Note 10), using several drops of nitric acid in excess. Boil the solution to expel oxides of nitrogen. Transfer the solution quantitatively to a 250 ml. volumetric flask and dilute with water to the mark (Note 11). Using several different aliquots of the standard solution, develop the color as described in the above procedure, measure the transmittancy at 540 millimicrons, and plot the calibration curve.

Range

The optimum range is about 1 to 8 p.p.m. of nickel, corresponding to 0.05 to 0.04 mg. of nickel per 50 ml. of the solution measured.

Notes

1. Aliquots of 5 ml. to 1 ml. of the composite solution are suitable for samples containing about 0.02% to 0.2% of nickel.

2. Cooper has shown that when manganese is present in large amounts relative to nickel, the amount of sample in the solution for color development should be decreased; he has also proposed an empirical correction for manganese on the apparent amount of nickel found.

3. According to Cooper, a copper to nickel ratio of about 3:1 can be tolerated if the transmittancy of the final solution is measured within ten minutes after preparation. Steels containing more than the tolerance amount of copper are not often encountered. When a large amount of copper is present, it should be separated by hydrogen sulfide precipitation from acid solution by the conventional method; after removing the precipitated copper sulfide and boiling out the hydrogen sulfide from the filtrate, it is then color developed as given in the procedure. Because of the effect of copper on the rate of fading of the nickel color, removal of copper even when present in less than 3:1 ratio to nickel is recommended for work of highest accuracy. Cooper gives an empirical correction for copper on the apparent amount of nickel found.

4. Ammonium citrate complexes the iron and other constituents which would otherwise precipitate with ammonium hydroxide.

5. Iodine oxidizes the nickel(II) to a higher oxidation state, which gives a red complex with the dimethylglyoxime. Although some procedures use bromine as the oxidizing agent, iodine has been found superior to bromine for this purpose.

6. By Cooper's procedure the dimethylglyoxime solution is added before the iodine solution; when this order of addition is used, the red precipitate of nickel(III) dimethylglyoximate occasionally forms. By effecting the oxidation first, precipitation is prevented.

7. The transmittancy of the solution is constant for 20 to 30 minutes when only nickel is present. When copper is present, fading of the color after about 15 minutes becomes significant, the effect being proportional to the amount of copper. Up to 10 minutes after processing the solution, the transmittancy is stable.

8. The color system has an absorption band at 540 millimicrons, and a somewhat stronger absorption at about 440 millimicrons. Cooper states that the 540 millimicron wavelength is used to avoid the interference of ferric citrate, which has almost no absorption at 540 millimicrons but considerable absorption at 440 millimicrons. However, by the blanking procedure used, the absorption due to ferric citrate would be cancelled out. Although the absorption at 440 millimicrons is stronger than that at 540 millimicrons, measurements at the latter wavelength provide a very sensitive method (optimum range about 1 to 8 p.p.m. of nickel), so that higher sensitivity is scarcely needed. The absorption band at 540 millimicrons is somewhat broader than that at 440 millimicrons,

hence any slight error in setting the wavelength scale is less significant at 540 millimicrons than at 440 millimicrons.

9. Use of aliquots of a single sample, rather than several smaller samples of different weights of a high-nickel steel, is recommended to avoid the large relative errors of weighing small samples.

10. Complete oxidation of the iron is usually indicated by rapid increase in the rate of evolution of oxides of nitrogen.

11. If desired, a further volumetric dilution (e.g., 1:10) of this solution may be made to provide suitable aliquots for color development.

6.7. DETERMINATION OF PHOSPHORUS

The method of analysis given below is essentially that of Hague and Bright, and is based upon the blue color of reduced phosphomolybdic acid.

Reagents

Ammonium molybdate solution: add 300 ml. of concentrated sulfuric acid to 500 ml. of water, and cool to room temperature; dissolve 20 g. of ammonium molybdate in the sulfuric acid solution and dilute with water to one liter.

Hydrazine sulfate solution: dissolve 1.5 g. of hydrazine sulfate in one liter of water.

Perchloric acid.

Potassium dihydrogen phosphate, KH_2PO_4 .

Sodium sulfite solution: dissolve 100 g. of anhydrous sodium sulfite in water and dilute to one liter.

Ammonium molybdate-hydrazine sulfate-sodium sulfite reagent: dilute 25 ml. of the ammonium molybdate solution to 60 ml. with water, add 10 ml. of the hydrazine sulfate solution and 20 ml. of the sodium sulfite solution, and dilute to 100 ml. with water. This mixed reagent must be prepared immediately before use.

Procedure

Transfer a suitable aliquot (Note 1) of the sample solution to an Erlenmeyer flask, add 5 ml. of perchloric acid, and heat until the acid fumes condense freely in the neck of the flask, and then for two minutes longer (Note 2). Cool the mixture, add 10 ml. of water and 15 ml. of sodium sulfite solution (Note 3), then boil the solution for 1 to 3 minutes. Cool to room temperature or below (Note 4), and add 20 ml. of the ammonium molybdate-hydrazine sulfate-sodium sulfite reagent (Note 5). Transfer the mixture quantitatively to a 50 ml. volumetric flask, dilute with water to the mark, and mix thoroughly. Using a pipet, transfer 25 ml. of the solution to a large test tube and immerse it in boiling water; after the water in the bath resumes boiling, continue the heating for exactly 9 minutes for full development of the blue color. Cool to room temperature, and measure the transmittancy at 820 millimicrons, using as a blank the remainder of the phosphorus solution which has not been heated. Calculate the phosphorus content of the steel by reference to the calibration curve.

Calibration

Weigh out 0.4390 g. of pure potassium dihydrogen phosphate, dissolve it in water, and make up volumetrically to 500 ml. The solution contains 200 p.p.m. of phosphorus, or 0.200 mg. of phosphorus per ml. Prepare standard solutions of lower concentration, as needed, by volumetric dilution (Note 6). Using several different aliquots of standard solution, develop the color by the procedure given above, measure the transmittancies against a similar blank, and construct the calibration curve.

Range

The optimum range is about 0.1 to 1 p.p.m. of phosphorus, which corresponds to about 0.005 to 0.05 mg. of phosphorus per 50 ml. of the solution measured.

Notes

1. For the amount of phosphorus commonly encountered in steels, an aliquot of 5 or 10 ml. of the composite sample solution is suitable.
2. The fuming period with perchloric acid is required to insure complete oxidation of phosphorus to phosphate.
3. Sodium sulfite is for the purpose of reducing iron(III) to iron(II).
4. Prompt cooling to room temperature or below is necessary to prevent some color development in the blank.
5. The mixture of reagents must be prepared immediately before use, otherwise maximum color may not develop.
6. An alternate method of calibration may be based upon a standard steel; because the phosphorus content of many steels is quite low, addition of known increments of standard phosphate solution may be required to avoid the use of large samples. In practice, it has been found that calibration by the use of only the standard phosphate solution has given good agreement with the certified phosphorus content of NBS standard steels.

6.8. DETERMINATION OF VANADIUM

The method is based upon the yellow to orange color produced by reaction of vanadate with hydrogen peroxide.

Reagents

For the determination:

Hydrochloric acid, approximately 7 molar: add 600 ml. of the concentrated acid to 400 ml. of water.

Hydrogen peroxide, 3%.

Isopropyl ether.

Perchloric acid.

Sodium chloride.

For the standardization (Method 2):

Ammonium persulfate solution, 15%, freshly prepared as needed.

Ammonium vanadate.

Ferrous ammonium sulfate solution, approximately 0.1 N: dissolve 40 g. of $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ in a liter of 5% sulfuric acid.

Hydrochloric acid.

Potassium ferricyanide solution, 0.1%, freshly prepared from solid $\text{K}_3\text{Fe}(\text{CN})_6$ in small quantity as needed.

Potassium permanganate standard solution, approximately 0.05 N, prepared and accurately standardized against primary standard sodium oxalate by the conventional method.

Sulfuric acid, 5%.

Procedure

Transfer a suitable aliquot (Notes 1, 2) of the sample solution to a separatory funnel, add water to bring the volume to 30 ml. and add 35 ml. of concentrated hydrochloric acid (Note 3). Add 50 ml. of isopropyl ether (Note 4), shake the funnel vigorously for 1 to 2 minutes, then allow the funnel to stand until the layers are well separated. Draw off the aqueous (lower) layer containing the vanadium into a beaker. To the ether solution in the funnel, add 10 ml. of 7 M hydrochloric acid, shake well, let stand for separation, and draw off the aqueous layer, combining it with the first solution (Note 5). Evaporate the solution containing the vanadium to about one-half its original volume. Add 10 ml. of perchloric acid, and evaporate to copious fumes (Note 6). To the hot mixture, add solid sodium chloride in small portions until about one gram has been added, and continue the fuming until all chromyl chloride has been volatilized (Note 7). Cool the solution and transfer it quantitatively to a 25 ml. volumetric flask. To the sample for measurement, add 2 ml. of 3% hydrogen peroxide (Note 8) and make up to the mark with water; for the blank, omit the hydrogen peroxide and dilute the solution to volume with water. Measure the transmittancy of the peroxidized solution at 460 millimicrons (Note 9) and compute the vanadium content of the sample by reference to the calibration curve.

Calibration

Method 1. The calibration may be made by the use of a standard steel of relatively high vanadium content (such as NBS Chromium-Vanadium Steel 30d). To several samples of various weights add 1:2 nitric acid, in small portions and with heating as necessary, to complete dissolution. Add 2 ml. of concentrated hydrochloric acid, and evaporate the mixture to a volume of a few milliliters. Transfer the solution to a separatory funnel, using 50 to 60 ml. of 7 M hydrochloric acid for transfer rinsing. Starting with the addition of isopropyl ether, carry the samples through the procedure given above; a steel sample carried through all the steps except for peroxidation is used as a blank for the transmittancy measurements. Plot the data in the usual way.

Method 2. A solution of ammonium vanadate, after proper standardization, can be used for calibration. Dissolve about 2.5 g. of ammonium vanadate in one liter of water (Note 10). The following standardization should be done to at least triplicate satisfactory checks. By pipet, transfer 50 ml. of the solution to a 500 ml. Erlenmeyer flask containing about 200 ml. of 5% sulfuric acid. Add potassium permanganate solution dropwise until the solution is faintly pink. With constant stirring add ferrous ammonium sulfate solution (Note 11) until a test drop of the mixture gives an immediate blue color with a drop of potassium ferricyanide solution on a spot plate, then 3 to 5 ml. more of the ferrous solution. Stir the solution for about a minute, add 8 ml. of freshly made ammonium persulfate solution (Note 12), and stir vigorously for one minute. Titrate with the standard potassium permanganate solution to a faint pink color which persists for 30 seconds. From the titration data, calculate the concentration of the ammonium vanadate solution in terms of vanadium (Notes 13, 14). Appropriate aliquots of the standard vanadium solution are taken for color development; transfer the aliquot to a 50 ml. volumetric flask, add 10 ml. of perchloric acid, 2 ml. of 3% hydrogen peroxide, and add water to the mark; prepare a similar blank, omitting the hydrogen peroxide. Measure the transmittancy at 460 millimicrons. Plot the calibration curve in the usual way.

Range

The optimum range is about 20 to 140 p.p.m. of vanadium, corresponding to 0.5 to 3.5 mg. of vanadium in 25 ml. of solution measured.

Notes

1. Because the vanadium content of many steels is quite low and the peroxide method is not highly sensitive, it is often more convenient to dissolve a separate sample of steel, of such size as required for the proper concentration range.

2. A similar aliquot of the sample solution, to be used for the blank, should be carried through the procedure, omitting the hydrogen peroxide.

3. This amount of concentrated hydrochloric acid gives a mixture which is about 7 M. Quantitative extraction of iron is attained from solution in which the range is about 6 M to 8.5 M in hydrochloric acid.

4. Isopropyl ether is superior to diethyl ether because of its lower solubility, lower volatility, and wider range of hydrochloric acid concentration over which extraction of iron is complete.

5. A single pass with the ether will remove about 99% of the iron, and 80% to 90% of any molybdenum which is present. Removal of iron is required because, if present in the final solution, it catalyzes the decomposition of hydrogen peroxide, with troublesome bubble formation in the absorption cells during transmittancy measurement. The isopropyl ether layer is discarded.

6. This procedure oxidizes any chromium(III) to chromium(VI) so that it can be volatilized as chromyl chloride. The perchloric acid also insures oxidation of vanadium to the +5 state required for rapid color development with hydrogen peroxide.

7. Chromyl chloride is a red-brown vapor; continue heating for one or two minutes after the red-brown vapors have disappeared.

8. Alternatively, 0.2 ml. of 30% hydrogen peroxide may be used. In either case, a measuring pipet is convenient. Caution: 30% hydrogen peroxide will cause severe skin burns.

9. At 460 millimicrons, peroxidized titanium absorbs strongly, hence titanium must be absent. If titanium were present in the solution, it could be separated by precipitation with phenylarsonic acid, as in the analysis of aluminum samples, Section 7.10. Molybdenum in peroxidized solution absorbs only feebly at 460 millimicrons, and molybdenum is largely removed by the ether extraction.

10. The ammonium vanadate generally available is not of sufficient purity to serve as a direct standard, hence its standardization is necessary. A solution containing about 2.5 g. of ammonium vanadate per liter contains approximately one gram of vanadium per liter, or about 1000 p.p.m. of vanadium.

11. Vanadium can also be reduced by bubbling sulfur dioxide gas through the solution. Excess sulfur dioxide is then removed by sweeping it out of the solution with carbon dioxide gas, and the solution is titrated with standard potassium permanganate.

12. Ammonium persulfate oxidizes the excess ferrous salt, otherwise it would be titrated along with the reduced vanadium. Persulfate does not oxidize the reduced vanadium in the absence of silver ion catalyst.

13. The vanadium content is readily given by the following:

$$\frac{\text{ml. of KMnO}_4 \times N \text{ of KMnO}_4 \times 50.95}{\text{ml. of ammonium vanadate solution taken}} = \text{mg. of vanadium per ml.}$$

14. If desired after the solution is standardized, a measured volume of the solution can be volumetrically diluted to give a solution of convenient integral vanadium content, e.g., 500 p.p.m. = 0.500 mg. per milliliter.

6.9. DETERMINATION OF SILICON

Various methods for silicon, applied to aliquots of the solution for the composite analysis, have not given satisfactory reproducibility. The failure may be associated with the use of the large sample required for the composite solution, and the longer treatment with hot acid to effect sample dissolution, with accompanying dehydration and precipitation of silicic acid. Satisfactory results are obtained by the use of separate smaller samples of steel. The method of Hill, with minor modifications, is used; the yellow color of molybdisilicic acid is measured.

Reagents

Nitric acid, 1:4.

Potassium persulfate, saturated aqueous solution (about 7%).

Sodium fluoride, 2.4% aqueous solution.

Sodium molybdate, 12% aqueous solution: dissolve 120 g. of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ in water and dilute to one liter.

Procedure

Weigh steel samples of 0.500 g. into 250 ml. Erlenmeyer flasks. Add 50 ml. of 1:4 nitric acid, and warm on a hot plate to hasten dissolution (Note 1). To the boiling solution, add 10 ml. of the potassium persulfate solution (Note 2), and boil until the solution clears (about one minute). Cool the flask and contents, transfer the solution to a 250 ml. volumetric flask and dilute to volume with water; mix the solution thoroughly. Transfer 25 ml. aliquots of the solution to dry beakers or flasks; one portion is to be used for the blank. To the blank, add 10 ml. of sodium fluoride solution (Note 3), and to the sample solution add 5 ml. of sodium molybdate solution (Note 4). After 10 minutes (Note 5) add 5 ml. of sodium molybdate solution to the blank, and 10 ml. of sodium fluoride solution to the sample. If slight turbidity develops in the sample solution, it usually disappears in 2 or 3 minutes. Without delay (Note 6) transfer the sample and the blank to plastic absorption cells (Note 7), and measure the transmittancy at 375 millimicrons (Note 8). Calculate the silicon content of the sample by reference to the calibration curve.

Calibration

Because of difficulties in the preparation and storage of standard silicate solutions, their use for calibration is impractical. One-half gram standard samples (Note 9) of different silicon content are easily obtained by weighing appropriate proportions of a high-silicon steel (such as NBS standard sample 12e, 21d, 32d, etc.) and of a sample containing little silicon (such as NBS standard sample 55c or 129a). The samples are dissolved and the color is developed as given in the above procedure, and the data used for construction of the calibration curve.

Range

The optimum range for measurement at 375 millimicrons is about 1 to 8 p.p.m. of silicon, corresponding to 0.025 to 0.20 mg. of silicon per 25 ml. of the solution measured.

Notes

1. Prolonged heating of the acid solution after dissolution is complete should be avoided.
2. Hill's procedure uses 5 ml. of 12% solution of ammonium persulfate; 10 ml. of saturated potassium persulfate provides about the same oxidizing capacity.
3. The concentration of fluoride is not critical, but the same amount must be added to all solutions. Even when stored in plastic bottles, a turbidity sometimes develops in the sodium fluoride solution. In this event, the solution must be filtered or, preferably, a fresh solution prepared.
4. Ammonium molybdate solution is specified in Hill's procedure. In testing the method, it was found that reproducibility of results was not especially good; however, by using sodium molybdate instead of ammonium molybdate satisfactory precision was attained. Because the difference in results appeared to be associated with ammonium ion, potassium persulfate was used instead of ammonium persulfate for the oxidizing agent in the previous step.
5. By the reverse order of addition of reagents to sample and to blank, development of color in the blank is prevented; sufficient time must be allowed for the fluoride to complex the silicate before addition of molybdate.
6. Maximum color intensity develops within about 5 or 6 minutes after the addition of molybdate, and the color is stable for a considerable period of time. However, for high silicon contents the blank slowly develops color while the sample fades slowly. For these reasons the measurement should be made without undue delay, that is, within 15 to 20 minutes after addition of the molybdate reagent to the sample solution and fluoride reagent to the blank solution. The blank may be stabilized by the presence of 0.1% citrate in the fluoride solution.
7. Prolonged use of fluoride solutions in glass absorption cells may subject them to considerable attack. Plastic absorption cells for the Beckman spectrophotometer are available from the manufacturer of the instrument. Caution: do not allow organic liquids, such as acetone, carbon tetrachloride, esters, etc., to contact the plastic cells.
8. Hill's directions specify transmittancy measurements "at 400 to 410 millimicrons." Using a Coleman Model 11 spectrophotometer, Hill reports that the molybdisilicate complex has a broad absorption band with maximum at 330 millimicrons. Previously, Schwartz and Morris reported that the most sensitive band for the measurement is at 410 millimicrons if conformity to Beer's law is the criterion. (By standard series methods of analysis, conformity to

Beer's law is not required.) It should be remarked that these investigators used filter photometers in which the filters passed wide bands of radiation, and a Coleman spectrophotometer without specifying whether the narrow or the wide slit was used. By the use of a Beckman spectrophotometer, with which narrow spectral bands are obtained, the molybdisilicate system shows a very sharp band centering at 355 millimicrons, the absorption changing very rapidly from 355 to the vicinity of 425 millimicrons. There is no indication of a "broad absorption band with maximum at 380 millimicrons," nor "a sensitive band at 410 millimicrons." These incorrect conclusions are no doubt the result of the wide bands passed by the filters and by the Coleman instruments used in the former work, and the fact that the region 355 to 425 millimicrons is on the side of a sharp absorption band. Measurements at 355 millimicrons on the Beckman instrument with tungsten filament source and Corex glass cells require large slit widths to balance the blank, and experience showed that poorer precision resulted at this wavelength than at somewhat longer wavelengths. Good reproducibility was attained, at satisfactory sensitivity, at 375 millimicrons; this is in general agreement with Hill's conclusion that accurate measurements may be made below 400 millimicrons. It should be emphasized that because the region 355 to 425 millimicrons is on a steep portion of the spectral curve, great care must be exercised in making the wavelength setting; a one millimicron error in wavelength setting in this region results in an error of about 1% transmittancy and produces a relative error of about 3% on the concentration of silicon represented. It should be remarked, in agreement with Hill's conclusions, that any wavelength in the region about 365 to 425 millimicrons can be used, at somewhat different sensitivities and concentration ranges. Unusual care must be exercised to establish the calibration curve by the use of several replicate samples for each of several calibration points.

9. By the use of samples of the same size, for both calibration and determination, the constituents (especially iron) other than silicon are present in similar amounts. The blanking procedure also effectively compensates for any absorption effects of the other constituents.

SECTION VII

PROCEDURE FOR ANALYSIS OF ALUMINUM ALLOYS

See the first part of Section VI, p. 24, for some comments about reagents and technique.

7.1. DISSOLUTION OF SAMPLE

Reagents

Nitric acid.
Perchloric acid.
Sodium hydroxide, 20% aqueous solution.

Procedure

Weigh accurately a 10.00 g. sample of the aluminum alloy (Note 1). Place 100 ml. of 20% sodium hydroxide (Note 2) in an 800 ml. beaker provided with a cover glass, and add the sample in small portions (Note 3); when all the sample has been added and the reaction has subsided somewhat, boil the mixture gently until reaction has ceased (10 to 15 minutes usually required). Separate the solution and residue by either of the following methods (Note 4).

Method 1. Transfer the mixture (Note 5) to a 250 ml. centrifuge bottle (Note 6), and settle the precipitate well by centrifugation (Note 7). Remove the supernatant liquid (Note 8). Wash any residue in the reaction beaker with about 30 ml. of water, pour off the wash water into the centrifuge bottle, stir up the residue in the bottle, and again settle the solids by centrifugation. Remove the wash liquid (Note 8), and repeat the washing operation one or two times. Using about 40 ml. of nitric acid, preferably hot, and about 20 ml. of water, transfer the material from the centrifuge bottle back to the original reaction beaker containing the residue from decantation washing.

Method 2. Dilute the mixture to 400 or 500 ml. with hot water. allow the residue to settle, and filter the hot solution by decantation through 15 cm. Whatman No. 54 paper (Note 9); wash the residue in the beaker several times with small portions of hot water, pouring the wash water off through the filter paper (Note 8). Open the filter paper and stick it to the inside wall of the original reaction beaker containing most of the residue. With a stream of water from a wash bottle, flush the residue off of the paper into the beaker. Heat about 40 ml. of nitric acid nearly to boiling, and drip the hot acid over the filter paper to dissolve any residue remaining on it. Wash the paper well with a fine stream of water.

Boil the mixture, from either of the above separation procedures, until the dark residue dissolves. Some samples may contain a dense white precipitate at this point; in this case, add perchloric acid in small portions until the precipitate dissolves; a maximum of 10 ml. of perchloric acid should be used (Note 10). Transfer the solution to a 250 ml. volumetric flask, dilute to volume, and mix thoroughly.

Notes

1. The sample weight to be taken, and the final volumetric dilution of the sample solution, may be varied from the values given, depending upon the content of the elements to be determined (if this be approximately known in advance) and upon the number of replicate analyses to be made for each constituent by the use of aliquots of the composite solution. For the determination of constituents that are encountered only in very small amounts, it is probably advantageous to dissolve a separate smaller sample (e.g., 1 or 2 g.) and use the entire solution for the determination of the desired constituent without having to take large aliquots of a volumetrically prepared solution.

2. Aluminum alloys can also be attacked directly with acid, using first hydrochloric acid until most of the sample is dissolved, and then nitric acid. Although this method of attack will provide a solution of the sample in a shorter time than the procedure given, there is an advantage in separating the aluminum by a first attack by alkali. Furthermore, if hydrochloric acid attack were used, it would then be necessary, before using aliquots of the solution for certain determinations, to remove the chloride by fuming down with other acids. For certain determinations in which chloride does not interfere, and especially for cases where the entire solution of a smaller sample is to be used, there is a time advantage in dissolving the sample by acid attack.

3. By adding the sample to the reagent, rather than the reverse, the dissolution can be accomplished more rapidly and with better control to prevent too vigorous frothing.

4. If only a very few samples are to be handled at a time, separation by centrifugation is probably advantageous. For routine work involving a large number of samples, a battery of several filters can be operated advantageously.

5. It is not necessary, nor even desirable, to make a quantitative transfer of the precipitate; washing by decantation is more efficient.

6. If Pyrex centrifuge bottles are used, transfer the mixture while hot.

7. It is absolutely imperative that centrifuge bottles be balanced by weighing to prevent vibration of the centrifuge.

8. The alkaline solution contains the aluminum, for which analysis is not made. Vanadium divides between the alkali-soluble portion and the residue, hence its analysis must be made on a separate sample which is attacked by acid. Zinc will be found in the alkaline solution; in the present investigation the sharpness of separation of zinc by alkali attack was not studied. For these reasons the alkaline solution and washings are discarded.

9. The paper to be used must have high wet strength and resistance to strong alkali as well as to hot nitric acid.

10. If a small amount of finely divided flocculent precipitate remains (probably silicic acid), dilute to 100 ml., add a small amount of paper pulp, and filter through a Whatman No. 54 paper, receiving the filtrate and washings in the 250 ml. volumetric flask.

7.2. DETERMINATION OF CHROMIUM

The method is essentially the same as that given for the determination of chromium in steel, Section 6.2, and is based upon the color of dichromate.

Reagents

Perchloric acid.

Ferrous perchlorate solution: dissolve 325 g. of $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in water and dilute volumetrically to 500 ml. 1.0 ml. = 0.10 g. of iron.

Procedure

Transfer a suitable aliquot of the sample solution from procedure 7.1 to an Erlenmeyer flask, add 10 ml. of the ferrous perchlorate solution (see Section 6.2, Note 5, p. 27), 20 ml. of perchloric acid, and continue exactly as described in Section 6.2 for the determination of chromium in steel.

Calibration

The same calibration curve used for chromium in steel can also be used for chromium in aluminum samples. The method may also be calibrated by the use of a standard solution of potassium dichromate. A solution containing 2.828 g. of pure $\text{K}_2\text{Cr}_2\text{O}_7$ made up volumetrically to one liter (or any identical weight to volume ratio) contains one milligram of chromium per milliliter (1000 p.p.m.); a 1:10 volumetric dilution of the stock solution gives a suitable working solution, from which several aliquots are carried through all steps of the above procedure. The calibration curve is constructed as usual.

Range

The optimum range is about 2 to 16 p.p.m. of chromium, corresponding to 0.1 to 0.8 mg. of chromium per 50 ml. of the solution measured.

7.3. DETERMINATION OF COPPER

The determination is based upon the color of copper benzoinoximate in chloroform solution, following essentially the procedure given by Dunleavy, Wiberley and Harley.

Reagents

Alpha-Benzoinoxime (Eastman No. 1877). 0.5% solution in 10% sodium hydroxide solution.

Chloroform.

Sodium hydroxide, 10% aqueous solution.

Sodium potassium tartrate (Rochelle salt): dissolve 300 g. of the solid in 500 ml. of water.

Procedure

Using a suitable aliquot of the sample solution (see below for Range), proceed exactly as in Section 6.3, p. 28, for the determination of copper in steel.

Calibration

The same calibration curve used for copper in steel can be used for copper in aluminum samples. The method may also be calibrated by the use of a standard copper solution. Dissolve 1.000 g. of pure (electrolytic) copper metal in the minimum amount of 1:1 nitric acid, transfer the solution quantitatively to a one liter volumetric flask, and dilute to volume with water. The solution contains 1 mg. of copper per ml. (1000 p.p.m.). A 1:10 volumetric dilution of the stock solution (e.g., 25 ml. to 250 ml.), containing 100 p.p.m. of copper, is a suitable working standard solution. Several aliquots, to cover the range of the method, are carried through all steps of the procedure, and the calibration curve constructed in the usual way.

Range

The optimum range is about 2 to 16 p.p.m. of copper, corresponding to 0.1 to 0.8 mg. of copper per 50 ml. of the solution measured.

7.4. DETERMINATION OF IRON

The determination is based upon the red color produced by reaction of ferrous salts with ortho-phenanthroline, following essentially the method of Saywell and Cunningham; a similar method is given by Fortune and Mellon.

Reagents

Acetate buffer mixture: dissolve 140 g. of sodium acetate trihydrate, $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$, in water, add 60 ml. of glacial acetic acid, and dilute to one liter. The mixture is approximately one molar in each solute.

Hydroxylamine hydrochloride (Eastman No. 340), 1% aqueous solution.

Nitric acid, 1:2.

Ortho-Phenanthroline, 0.2% aqueous solution. (Also called 1,10-phenanthroline; obtainable as the monohydrate, $\text{C}_{12}\text{H}_8\text{N}_2 \cdot \text{H}_2\text{O}$, from G. Frederick Smith Chemical Company, Columbus. Ohio.)

Lead metal, fine granules, free from iron.

Procedure

Transfer a suitable aliquot (Note 1) of the sample solution to a small beaker, and add water if necessary to make a volume of about 25 ml. Add about 2 g. of iron-free granulated lead, and heat the mixture, with frequent stirring, to precipitate the copper (Note 2). Cool to room temperature, and filter off the copper and excess lead; receive the filtrate directly in a 100 ml. volumetric flask. Wash the filter paper with small portions of water, adding the washings to the main solution, and dilute the solution to volume. Transfer identical aliquots (Note 1) of this solution to each of two 50 ml. volumetric flasks; to each flask add 2 ml. of the hydroxylamine hydrochloride solution (Note 3) and 5 ml. of acetate buffer mixture (Note 4). To one sample (for measurement) add 5 ml. of ortho-phenanthroline solution, and dilute with water to the mark. Dilute the other sample (to be used as the blank) to volume; do not add ortho-phenanthroline to the blank. Measure the transmittancy at 510 millimicrons, and calculate the iron content by reference to the calibration curve.

Calibration

Weigh 1.000 g. of pure iron (primary standard quality; "iron wire for standardizing" is recommended), and dissolve it in the minimum amount of 1:2 nitric acid, warming as necessary. Transfer the solution quantitatively to a one liter volumetric flask, add 5 ml. of nitric acid, and dilute to volume with water; mix thoroughly. The solution contains 1 mg. of iron per ml. (1000 p.p.m.). A 1:10 volumetric dilution (e.g., 25 ml. to 250 ml.) of the stock solution is a suitable working standard. Several aliquots of different size are used for data for the calibration points. Transfer identical aliquots to small beakers, add 10 ml. (Note 5) of 1% hydroxylamine hydrochloride solution, and heat for 5 to 10 minutes. Transfer the solutions quantitatively to 50 ml. volumetric flasks; add 5 ml. of acetate buffer mixture, and continue from this point exactly as given in the procedure above, developing one

solution with ortho-phenanthroline and using the other for a blank. From the measured transmittancies at 510 millimicrons and the known iron content, construct the calibration curve in the usual way.

Range

The optimum concentration range is about 0.5 to 4 p.p.m. of iron, or 0.025 to 0.20 mg. of iron per 50 ml. of the solution measured.

Notes

1. The reaction is very sensitive for iron; for some samples it may be desirable to make a volumetric dilution of a portion of the composite sample solution for this determination. Provision for division of the sample by aliquoting is also made after the removal of copper.

2. In addition to replacing copper from solution, metallic lead also effects reduction of iron(III) to iron(II). The solution should be heated for five minutes or longer, the time required being somewhat dependent upon the copper content of the sample.

3. Hydroxylamine hydrochloride completes the reduction of iron to the ferrous state, and prevents its atmospheric oxidation. The ortho-phenanthroline reagent gives the red color with iron only in the ferrous state.

4. The color does not develop in strong acid solution, but within the pH range of 2 to 9 a stable color is produced.

5. In the standardization, the solution is not treated with lead as in the analysis, hence a larger amount of hydroxylamine hydrochloride is required to insure complete reduction of the iron.

7.5. DETERMINATION OF MANGANESE

The method is based upon the color of permanganate, formed by oxidation with periodate (method of Willard and Greathouse).

Reagents

Phosphoric acid.
Potassium nitrite, 2% aqueous solution.
Potassium periodate (meta), KIO_4 .

Procedure

Treat aliquots of the sample solution exactly as given in procedure 6.4, p. 30, for the determination of manganese in steel.

Calibration

The same calibration curve prepared for the determination of manganese in steel may be used for the determination of manganese in aluminum. The calibration also may be made by the use of alloys of aluminum relatively high in manganese (such as NBS standard sample 35a, 0.66% manganese). Several separate samples, to cover the appropriate range (or aliquots of a single larger sample brought to known volume) may be used. Treat the weighed sample with the minimum amount of 20% sodium hydroxide solution to complete reaction, cool the mixture, neutralize with 1:1 nitric acid, then add 1 or 2 ml. of nitric acid in excess. Starting with the addition of phosphoric acid, continue exactly as in the analysis procedure given in Section 6.4, p. 30. From the measured transmittancy at 526 millimicrons and the known manganese content, construct the calibration curve as usual.

Range

The optimum concentration range is about 2 to 16 p.p.m. of manganese, corresponding to 0.2 to 1.6 mg. of manganese per 100 ml. of solution measured.

7.5. DETERMINATION OF MOLYBDENUM

Although the scope of the analyses contemplated by the contracting agency for this project included a method for molybdenum up to 1% in aluminum alloys, molybdenum is apparently met only rarely in aluminum samples. No standard samples of aluminum containing molybdenum are available from the National Bureau of Standards, nor were any molybdenum-bearing aluminum alloys furnished by the contracting agency for test purposes in this project. Although molybdenum metal is insoluble in hydrochloric acid, in dilute sulfuric acid, and in strong alkali, its behavior in alloys attacked by these reagents appears not to have been well established; it seems reasonable, on the basis of the above properties, to assume that molybdenum would be present in the alkali-insoluble portion of the alloy, which is then dissolved in nitric acid (Section 7.1, p. 44) to give the composite solution. If molybdenum is present in only minor amounts, a relatively large sample would be required, in which case it is probably better to dissolve an appropriate weight of the sample directly in perchloric acid and use the entire solution for the molybdenum determination by the thiocyanate method.

Reagents

Amyl acetate.

Hydrochloric acid.

Sulfuric acid, 1:6.

Sodium chloride.

Sodium thiocyanate, 10% aqueous solution.

Stannous chloride solution: dissolve 300 g. of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 200 ml. of hydrochloric acid, and dilute to one liter with water.

Procedure

If the original alloy is to be used, transfer a weighed sample of it to a 250 ml. beaker, add about 10 ml. of water and 5 to 10 ml. of perchloric acid (depending on the size of sample), and warm if necessary to facilitate dissolution. When the reaction subsides, boil the mixture down to perchloric acid fumes, add 1 g. of sodium chloride in small portions, and continue the fuming until all the chromyl chloride is expelled. Cool to room temperature.

Transfer the above solution, or a suitable aliquot of the composite solution from which chromium has been removed, to a small separatory funnel, and continue the determination by procedure 6.5, p. 31 (determination of molybdenum in steel).

Calibration

The same calibration curve used for molybdenum in steel may be used. Calibration may also be established by the use of a standard molybdenum solution. 1.500 g. of pure molybdic oxide, MoO_3 , dissolved in the minimum amount of ammonium hydroxide and diluted to exactly one liter, or 1.840 g. of pure ammonium heptamolybdate tetrahydrate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, dissolved

in water and made to one liter, yields a solution containing 1 mg. of molybdenum per ml. (1000 p.p.m.). A 1:100 volumetric dilution (e.g., 10 ml. to 1000 ml.) is a suitable working standard solution.

Range

The optimum range is about 0.5 to 5 p.p.m. of molybdenum, corresponding to about 0.0125 to 0.125 mg. of molybdenum in 25 ml. of the solution measured.

7.7. DETERMINATION OF NICKEL

Nickel is determined on the basis of the red color produced by reaction of ammoniacal dimethylglyoxime with nickel in its higher oxidation state, following a modification of the procedure given by Cooper. Extensive notes on the determination are given in Section 6.6.

Reagents

Ammonium citrate solution: dissolve 540 g. of the solid in water and dilute to one liter.

Ammonium hydroxide, 1:1.

Dimethylglyoxime, 0.1% ammoniacal solution: dissolve 1 g. of dimethylglyoxime in 500 ml. of concentrated ammonium hydroxide and dilute to one liter.

Hydrogen sulfide gas.

Iodine solution: dissolve 8 g. of potassium iodide and 2.5 g. of iodine in water and dilute to one liter.

Sodium hydroxide, 0.02% aqueous solution.

Sodium sulfide solution: saturate the required volume of 0.02% sodium hydroxide solution with hydrogen sulfide gas; prepare fresh as needed.

Sulfuric-phosphoric acid mixture: to 850 ml. of water add 75 ml. of sulfuric acid and 75 ml. of phosphoric acid.

Procedure

Use appropriate aliquots (Note 1) of the sample solution from procedure 7.1, p. 44; one portion is to be used for the blank. If copper is present in more than trace amounts (Note 2), treat the solution with about 20 ml. of freshly prepared sodium sulfide solution (Note 3). Stir well, and let stand for about 5 minutes to allow the precipitate to coagulate and settle. Filter off the copper sulfide (Note 4), and wash it several times with distilled water, receiving the filtrate and washings in a beaker. Boil the solution to expel hydrogen sulfide; cool, and transfer the solution quantitatively to a 50 ml. volumetric flask. Starting with the addition of 1 ml. of sulfuric-phosphoric acid mixture, continue the determination exactly as given in procedure 6.6, p. 33, determination of nickel in steel.

Calibration

The same calibration curve as used for nickel in steel may be used for nickel in aluminum. Alternatively, calibration may be made from a standard nickel solution. Dissolve 1.000 g. of pure nickel metal in 1:2 nitric acid, transfer the solution quantitatively to a one liter flask and dilute to the mark with water. The solution contains 1 mg. of nickel per ml. (1000 p.p.m.). A 1:100 volumetric dilution (e.g., 10 ml. diluted to 1000 ml.) is a convenient working standard solution. Aliquots are developed as in procedure 6.6, p. 33, starting with the addition of 1 ml. of sulfuric-phosphoric acid mixture. Plot the data in the usual way.

Range

The optimum range is about 1 to 8 p.p.m. of nickel, corresponding to 0.05 to 0.4 mg. of nickel per 50 ml. of the solution measured.

Notes

1. See Notes 1 and 2, p. 34.
2. See Note 3, p. 34. Because the copper to nickel ratio in the sample will not likely be even approximately known at this stage, routine procedure for removal of any copper is recommended. If copper is known to be present in only very small amounts, the sulfide treatment may be omitted.
3. The sodium sulfide solution must be freshly prepared. Alternatively, hydrogen sulfide gas may be bubbled through the sample solution to precipitate the copper as sulfide. For either reagent, the solution must be somewhat acid (the excess from the dissolution procedure is adequate), to prevent the precipitation of any nickel as sulfide.
4. An alternate procedure is to transfer an aliquot of the solution for analysis to a 100 ml. volumetric flask containing 20 ml. of the sodium sulfide solution, and make up to volume. Then filter some of the solution into a dry beaker, and take 25 ml. aliquots of the filtrate for continuation of the procedure; one such aliquot serves as the blank, prepared as given in the procedure on p. 33.

7.8. DETERMINATION OF TITANIUM

The determination is based upon the yellow to orange color produced by peroxidation of titanium solutions.

Reagents

For the determination:

Hydrochloric acid, 1:1.
Hydrogen peroxide, 3%.
Nitric acid, 1:1.
Sulfuric acid, 1:4.

For the standardization:

Ammonium hydroxide, 1:1.
Potassium acid sulfate, or potassium pyrosulfate.
Sulfuric acid.
Titanium dioxide.

Procedure

Transfer suitable aliquots (Note 1) of the solution for analysis to 100 ml. beakers; add 10 ml. of 1:4 sulfuric acid, and evaporate to a volume of about 10 ml. Cool the solution and transfer it quantitatively to a 50 ml. volumetric flask. For color development, add 2 ml. of 3% hydrogen peroxide, dilute with water to the mark, and mix thoroughly. To prepare the blank, omit the hydrogen peroxide, and dilute the solution to volume. Measure the transmittancy at 410 millimicrons, and calculate the titanium content of the sample by reference to the calibration curve.

If a separate sample of the alloy is to be used, transfer a weighed portion to a 400 ml. beaker, add 1:1 hydrochloric acid, warming as necessary, until reaction subsides, then add small portions of 1:1 nitric acid to complete the dissolution. Add 10 ml. of 1:4 sulfuric acid, and complete the determination as in the paragraph above.

Calibration

In a 500 ml. Erlenmeyer or Kjeldahl flask place about 2 g. of titanium dioxide (Note 2). Add 25 ml. of concentrated sulfuric acid, and heat the mixture in the direct flame of a burner almost to fuming. Add potassium acid sulfate (or the pyrosulfate), in about 0.5 g. portions from time to time while continuing the flame fuming, until the titanium dioxide has dissolved (Note 3). Cool the mixture to room temperature, add water to dissolve the solids (warming as necessary), and finally transfer the solution to a one liter volumetric flask and make up to volume with water; mix thoroughly. For standardization transfer three or four 50 ml. aliquots of the solution to separate 600 ml. beakers, add about 100 ml. of water, heat to boiling, and precipitate the titanium (as hydrous oxide) by adding 1:1 ammonium hydroxide slowly and with good stirring, until after blowing away the fumes from above the solution, it smells faintly of ammonia. Maintain the mixture near the boiling point for about 5 minutes, then filter the hot solution through a paper filter, finally

effecting complete transfer of the precipitate to the filter; wash the precipitate several times with hot water. Ignite the paper and contents in a previously ignited and weighed crucible, using finally the full temperature of a good gas burner. Cool to near room temperature, complete the cooling in a desiccator, and finally weigh. Repeat the ignition to constant weight. From the weight of the TiO_2 residue, calculate the titanium represented by it (Note 4) and the titanium content of the solution (Notes 5, 6). Suitable aliquots of the solution, or solutions of lower concentration made by volumetric dilution, are then color developed by the procedure on p. 55, and the calibration curve made as usual.

Range

The optimum range is about 5 to 50 p.p.m. of titanium, corresponding to 0.25 to 2.5 mg. of titanium in 50 ml. of the solution measured.

Notes

1. Peroxidized vanadium solutions also have a yellow color (maximum absorption at 460 millimicrons). When both titanium and vanadium are present (probably the usual case, although the amounts may be disproportionate), a separation may be required. The sensitivity of the vanadium reaction at 410 millimicrons, at which the peroxidized titanium is measured, is so much less than that of the titanium reaction that trace amounts of vanadium cause little interference with the determination of titanium. Except in special aluminum alloys such as aluminum hardener, these elements, especially vanadium, are found in quite small amounts (e.g., perhaps 0.002% vanadium and 0.01% to 0.03% titanium). Because of the low sensitivity and small content of desired constituent, a quite large aliquot of the composite solution would usually be required for titanium (e.g., 25 ml., representing 1 g. of a 0.02% titanium sample); for this reason, it is convenient to make the determination on a separate sample which has been attacked by acid. If vanadium is present in more than trace amounts, a separation of titanium from vanadium by procedure 7.10, p. 58, should be made.

2. Titanium dioxide is not available in purity sufficient for a primary standard. The quantity given is somewhat more than required to give a liter of solution corresponding to 1 g. (1000 p.p.m.) of titanium.

3. A titanium solution can also be prepared from potassium titanyl oxalate, $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$, which is decomposed and solubilized by fuming with sulfuric acid and ammonium sulfate. Common reference works may be consulted for details.

4. The factor for converting titanium dioxide to titanium is $47.90/79.90 = 0.5995$, or, for practical purposes, 0.600.

5. If desired, the proper volume of the standardized solution may be diluted to give a solution of some convenient integral concentration, such as 1000 p.p.m. or 500 p.p.m.

6. Standardization may also be made gravimetrically by precipitating the titanium with cupferron, or volumetrically by reducing the titanium and titrating it with standard ferric solution; details are given in common reference books.

7.9. DETERMINATION OF VANADIUM

The determination is based upon the yellow color produced by reaction of vanadate solutions with hydrogen peroxide.

Reagents

Hydrochloric acid, 1:1.
Hydrogen peroxide, 3%.
Nitric acid, 1:1.
Perchloric acid.
Sodium chloride.
Sulfuric acid, 1:4.

Procedure

Use a portion of the aluminum alloy (Note 1) for vanadium analysis; if titanium is present, follow procedure 7.10, p. 58. If titanium is known to be absent, transfer the weighed sample of the alloy (Notes 2, 3) to a beaker, add 1:1 hydrochloric acid until vigorous reaction has subsided, then 1:1 nitric acid, heating as necessary, to complete the dissolution. Add 5 to 10 ml. of perchloric acid, heat to fuming, add about 1 g. of sodium chloride, in small increments, and continue the fuming to volatilize the chromium as chromyl chloride. Cool to room temperature, transfer quantitatively to a 25 ml. volumetric flask, and add 2 ml. of 3% hydrogen peroxide to the sample for measurement (omit hydrogen peroxide from the blank); dilute with water to the mark and mix thoroughly. Measure the transmittancy at 460 millimicrons, and calculate the vanadium content by reference to the calibration curve.

Calibration

The same calibration curve used for vanadium in steel may be used.

Range

The optimum range is about 20 to 140 p.p.m. of vanadium, corresponding to 0.5 to 3.5 mg. of vanadium in 25 ml. of the solution measured.

Notes

1. In the procedure for dissolution of the sample, Section 7.1, p. 44, vanadium is found both in the solution and in the residue from the alkali attack; it must therefore be determined on the original sample.

2. Several grams may have to be taken to provide a vanadium content in the optimum range for measurement.

3. One sample, to serve as the blank, should be carried through in parallel with the determination, except that hydrogen peroxide is not added to the blank.

7.10. SEPARATION OF TITANIUM AND VANADIUM

Small amounts of vanadium cause only slight interference in the titanium determination because of the lower sensitivity inherent in the vanadium reaction and the fact that at 410 millimicrons, the wavelength for the titanium measurement, the spectral curve for peroxidized vanadium has very little overlap on the spectral curve for peroxidized titanium. Conversely, a small amount of titanium causes serious error in the determination of vanadium; at 460 millimicrons, the wavelength for the vanadium measurement, the spectral curve for peroxidized titanium overlaps that of the vanadium to a great extent. Therefore, the peroxide determination of vanadium in a solution also containing titanium is not valid, and a separation of these elements is required.

Reagents

Hydrochloric acid, 1:1.
Nitric acid, 1:1.
Perchloric acid.
Phenylarsonic acid (Eastman No. 2020), saturated aqueous solution (about 8%).
Sulfuric acid.
Sodium hydroxide, 10% aqueous solution.

Procedure

Place the weighed sample (1 g. or more) of the aluminum alloy in a beaker; attack it by treatment with 1:1 hydrochloric acid until the reaction subsides, then add 1:1 nitric acid, with heating as required, to complete the dissolution, and finally boil to expel oxides of nitrogen. Cool the solution and add 10% sodium hydroxide solution until, after good stirring, a small amount of precipitate just forms permanently. Add 4 ml. of 1:1 nitric acid (Note 1), and stir until all the precipitate dissolves. Add 50 ml. of phenylarsonic acid solution, stir well, and allow the mixture to stand several minutes for coagulation of the precipitate (Note 2). Filter off the titanium phenylarsonate onto a Whatman No. 40 paper (Note 3), and wash the precipitate several times with water to which a few drops of nitric acid and several drops of phenylarsonic acid solution have been added (Note 4).

Filtrate. To the filtrate containing the vanadium add 30 ml. of concentrated nitric acid and 10 ml. of perchloric acid, and heat to strong fuming to destroy the organic matter. Add 1 g. of sodium chloride, in small portions, and continue the fuming to completely expel chromium as chromyl chloride. Cool the solution, and develop and measure the vanadium color as directed in procedure 7.9, p. 57.

Precipitate. Transfer the precipitate (Note 5) to a beaker or flask, add 15 ml. of concentrated nitric acid and 5 ml. of concentrated sulfuric

acid, and heat to fuming to destroy organic matter. Cool the solution, and develop and measure the titanium color as directed in procedure 7.8, p. 55.

Notes

1. The separation with phenylarsonic acid should be made from solution containing dilute mineral acid; an excess of acid should be avoided, for it would prevent complete precipitation of the titanium.
2. Test for complete precipitation by adding a little more phenylarsonic acid solution, either to the supernatant liquid after the precipitate has settled, or to the first portion of the filtrate.
3. The filtrate and washings are reserved for the determination of vanadium; for convenience in the subsequent evaporation, receive the filtrate in a beaker.
4. If the precipitate settles well, washing by decantation is convenient, and it is not necessary to make a quantitative transfer of the precipitate to the filter.
5. Transfer of the precipitate is conveniently made by piercing the apex of the filter paper, and flushing off the precipitate, with a stream of water from a wash bottle, receiving the suspension in the same beaker in which the precipitation was made (see Note 4 above). Then drip the concentrated nitric acid over the filter paper, wash the paper with small portions of water, add the sulfuric acid to the mixture in the beaker, and proceed to the fuming. If complete removal of the precipitate from the paper is difficult, tear off the half of the paper holding the residue and put it in the acid solution to be fumed down; in this case, longer fuming and the addition of more nitric acid will probably be required.

7.11. DETERMINATION OF SILICON

The spectrophotometric determination of silicon in aluminum on the basis of the yellow color of molybdisilicic acid or the blue color of its reduction product has been the subject of many investigations. The results are markedly influenced by the method of attacking the sample, the pH of the solution, time interval between reagent addition and transmittancy measurement, presence of diverse ions, etc. During the course of this project many methods and modifications were tried (see references of Hadley; Hill; Carlson and Banks), but none was found that gave reproducible results. In the absence of a reliable spectrophotometric method, the procedure for gravimetric determination of silicon is given below.

Reagents

Hydrofluoric acid.
Nitric acid.
Perchloric acid, 2:1.
Sodium hydroxide, pellets.
Sulfuric acid, 1:1 and 1:99.

Procedure

Transfer the weighed sample (Note 1) to a nickel or monel metal beaker provided with a cover (Note 2). Add 1.5 g. of sodium hydroxide pellets for each gram of sample taken, then add cold water in small portions until violent reaction subsides; keep the beaker well covered to prevent loss. Wash down the cover and sides of the beaker with a minimum amount of hot water. Evaporate on a hot plate to syrupy consistency. Cool the mixture, add 10 ml. of water, and transfer it to a beaker containing 40 ml. of 2:1 perchloric acid. Rinse the reaction beaker with hot water, then with 10 ml. of 2:1 perchloric acid, and again with water, policing well. Add 5 ml. of nitric acid to the solution and evaporate to copious fumes, continuing the fuming for at least 10 minutes. Cool the mixture, add 100 ml. of hot water and some paper pulp, and stir well, heating as necessary to dissolve soluble salts. Filter the hot solution through Whatman No. 40 filter paper on which a little paper pulp has been placed. Use 1:99 sulfuric acid for transfer and washing; police the beaker thoroughly. Place the filter paper containing the silica in a previously ignited and weighed platinum crucible. Dry and char the paper carefully, add a drop of nitric acid, and complete the ignition at about 1100°C. for 30 minutes. Cool the crucible in a desiccator, and weigh as impure silica. Moisten the residue with a few drops of water, add 5 ml. of hydrofluoric acid (Note 3), two drops of sulfuric acid (Note 4), and evaporate carefully to dryness. Repeat the treatment with hydrofluoric acid and sulfuric acid, and finally ignite at 1100°C. for 10 minutes. Cool the crucible in a desiccator, and weigh. The difference in weights, after deducting the amount of the blank, represents silicon dioxide which was volatilized as the fluoride. Calculate the amount of silicon in the sample (Note 5).

Notes

1. The sample should, if practicable, be large enough that weighing errors on the amount of silica separated are relatively small. For high silicon content, samples of 2 to 5 g. are satisfactory; for samples low in silicon, a 10 g. sample should be used.

2. Vessels of glass, porcelain, or other silicate ware cannot be used for the alkaline attack on account of the introduction of silica. Vessels of nickel, monel metal, silver, or Fluorethane are satisfactory.

3. Reaction of hydrofluoric acid with silicon dioxide volatilizes it as silicon tetrafluoride.

4. Sulfuric acid is required to transpose any metal fluorides to their sulfates, which upon ignition give the oxides; this insures that such impurities are in the same weighing form after removal of the silica as before.

5. The factor for converting silicon dioxide to silicon is $28.06/60.06$
 $= 0.4672$.

APPENDIX I
SUMMARY OF METHODS

<u>Element</u>	<u>Method</u>	<u>Wavelength for transmittancy measurement, millimicrons</u>	<u>Optimum con- centration range for 1 cm. cells, p.p.m.</u>
Chromium	As dichromate, after oxidation with perchloric acid	380	2 - 16
Copper	Alpha-benzoinoxime, chloroform extract	440	2 - 16
Iron	Ortho-phenanthroline	510	0.5 - 4
Manganese	As permanganate, after oxidation with periodate	526	2 - 16
Molybdenum	Stannous chloride and sodium thiocyanate, amyl acetate extract	468	0.5 - 5
Nickel	Dimethylglyoxime, after oxidation with iodine	540	1 - 8
Phosphorus	Reduced phosphomolybdic acid	820	0.1 - 1
Titanium	Hydrogen peroxide	410	5 - 50
Silicon	As molybdisilicic acid	375	1 - 8
Vanadium	Hydrogen peroxide	460	20 - 140

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