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DETERMINATION OF NICKEL BY SPECTROPHOTOMETRIC
MEASUREMENT OF THE CHLOROFORM EXTRACT OF
NICKEL^{II} - DIMETHYLGLYOXIMATE-- APPLICATION TO
BRASSES, BRONZES, MAGNESIUM AND ALUMINUM
METALS AND THEIR ALLOYS

by

Elsie M. Penner* and W.R. Inman**

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SYNOPSIS

A spectrophotometric procedure involving chloroform extraction of nickel^{II} - dimethylglyoximate and direct photometric measurement of the extract at 370 m μ has been applied to the determination of 0.0005 to 1% nickel in brasses and bronzes and in magnesium and aluminum metals and their alloys. Copper and zinc are complexed with sodium thiosulphate prior to extraction of the nickel complex from an ammonium tartrate medium at pH 6.5. Manganese and other elements present in the materials described do not interfere in the proposed method.

* Scientific Officer and ** Head, Analytical Chemistry Subdivision, Mineral Sciences Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

Direction des mines

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DOSAGE DU NICKEL PAR LA MESURE SPECTROPHOTOMÉTRIQUE
DE L'EXTRAIT CHLOROFORMIQUE DU COMPLEXE NICKEL^{II}-
DIMÉTHYLGLYOXIME. APPLICATION AUX LAITONS,
AUX BRONZES, AINSI QU'AU MAGNÉSIUM, À
L'ALUMINIUM ET À LEURS ALLIAGES.

par

Elsie M. Penner* et W.R. Inman**

RÉSUMÉ

Un procédé spectrophotométrique qui comporte l'extraction au chloroforme du complexe nickel^{II}-diméthylglyoxime et la mesure photométrique directe de l'extrait à 370 m μ , a été appliqué au dosage du nickel en proportion de 0.0005 à 1% dans les laitons et les bronzes et dans le magnésium, l'aluminium et leurs alliages. Le cuivre et le zinc sont convertis en un complexe à l'aide de thio-sulfate de sodium avant l'extraction du complexe de nickel en milieu de tartrate d'ammonium au pH 6.5. La manganèse et les autres éléments présents dans les matériaux décrits ne nuisent en rien au procédé en cause.

*Chargé de recherches et **chef, Subdivision de la chimie analytique, Division des sciences minérales, Direction des mines, ministère des Mines et des Relevés techniques, Ottawa, Canada.

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INTRODUCTION

The Mines Branch laboratories are engaged in collaborative work with the National Bureau of Standards on the analysis of brasses and bronzes for use as spectrographic standards. As part of this project, the present investigation was undertaken to develop a spectrophotometric procedure that would be applicable to the determination of small amounts of nickel in all types of brass and bronze samples.

The majority of the spectrophotometric methods described in the literature for determining nickel in copper-base materials depend on alkaline oxidation of a nickel^{II} salt in the presence of dimethylglyoxime, to the orange-red nickel^{IV} complex, after a preliminary electrolytic removal of copper. However, this method is not suitable for the accurate determination of small quantities of nickel in brasses and bronzes unless provision is made for the removal of manganese and residual copper in the electrolyte, because these elements are known to interfere in the oxidation procedure (1).

A more direct method is that based on chloroform extraction of the nickel^{II} - dimethylglyoxime complex (2) and subsequent photometric measurement of the extract (3, 4). Although copper and manganese are reported to interfere in this method also, their respective interference effects can be eliminated with sodium thiosulphate (5) and hydroxylamine hydrochloride (6). Nielsch (7, 5) applied the above method in conjunction with the procedures described for eliminating copper and manganese interference, to the direct determination of nickel in copper alloys and copper salts. Later workers, Boltz et al. (8), Wiedmann (9) and Mohr (10), used modifications of Nielsch's procedure. However, the dissolution procedures described in all these papers were considered unsatisfactory for decomposing certain types of brass and bronze samples. In addition, insufficient data were presented to indicate the applicability of these methods to the determination of small amounts of nickel in a wide variety of brasses and bronzes.

Recently, Penner and Inman (11) reported a method for determining trace amounts of nickel in high-purity niobium, tantalum, molybdenum and tungsten metals, also based on the direct measurement of the absorbance of the chloroform extract of nickel^{II} - dimethylglyoximate. It was considered that this procedure could easily be adapted to the determination of nickel in brasses and bronzes, by modifying the extraction procedure to include complexing of copper with thiosulphate.

This report describes the successful application of the method of Penner and Inman (11) to the determination of small amounts of nickel in various types of brasses and bronzes. The method has also been extended to the determination of nickel in magnesium and aluminum metals and their alloys. The results obtained by the proposed method agree favourably with the certificate values for certain National Bureau of Standards and British Chemical Standards samples.

APPARATUS AND REAGENTS

Spectrophotometer: Beckman Model DU

pH Meter: Leeds and Northrup

Standard Nickel Solution

Dissolve 3.3647 g of nickel ammonium sulphate hexahydrate ($\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$) in water and dilute to 1 litre. Dilute 5 ml of this stock solution to 250 ml with water. Prepare fresh as needed; 1 ml of this diluted solution = 10 μg Ni.

Dimethylglyoxime, 1% Solution

Dissolve 5 g of dimethylglyoxime (British Drug Houses, Ltd.) in ethyl alcohol and dilute to 500 ml with ethyl alcohol.

Ammonium Tartrate, 20% Solution

Dissolve 200 g of ammonium tartrate in water and dilute to 1 litre.

Sodium Thiosulphate, 50% Solution

Dissolve 250 g of sodium thiosulphate in hot water, cool, and dilute to 500 ml.

Iron, 0.05% Solution

Dissolve 0.250 g of pure iron granules in 25 ml of concentrated hydrochloric acid and dilute to 500 ml.

Acid Mix

Add 500 ml of concentrated sulphuric acid to 1250 ml of water, cool, and add 350 ml of concentrated nitric acid.

Ammonium Sulphamate Tablets

Obtained from Eberbach Corporation, Ann Arbor, Michigan.

Chloroform

Analytical reagent.

Ethyl Alcohol

95%.

PROCEDURE

Calibration Curve

Add 5 ml of 20% ammonium tartrate solution to each of five 250-ml beakers. Then, by burette, add to the last four beakers 2.5, 5, 7.5 and 10 ml, respectively, of standard nickel solution (i.e., 1 ml = 10 µg Ni). Dilute the contents of each beaker to approximately 50 ml with water. The first beaker contains the blank. Add to each of the resulting solutions 5 ml of 50% sodium thiosulphate solution, and then, using a pH meter, adjust the pH of each solution to 6.5 ± 0.1 with 2:98 ammonia solution. Transfer the solutions to 125-ml separatory funnels and dilute to approximately 100 ml with water. (The stem of each funnel is first rinsed with ethyl alcohol to remove water droplets.) Then add to each funnel 5 ml of chloroform (graduated pipette) and 3 ml of dimethylglyoxime solution, stopper, and shake for 2 minutes. Allow 5 minutes for the layers to separate, then carefully drain the chloroform extract into a dry 25-ml volumetric flask. (Because of the high salt concentration of the aqueous phase, care must be taken that none of it accompanies the chloroform extract, otherwise the final ethyl alcohol solution of the extract will be turbid.) Re-extract the solution by shaking for 1 minute with 3 ml of chloroform and then for 30 seconds with 2 ml of chloroform. The last extraction serves to wash the aqueous layer and also the stem of the funnel. Combine these extracts with the first one, dilute to volume with ethyl

alcohol, and mix. Determine the absorbance of each of the resulting chloroform-ethyl alcohol solutions of nickel^{II} - dimethylglyoximate against the blank as the reference solution, using 5-cm cells at a wavelength of 370 m μ . Plot micrograms of nickel vs. absorbance.

General Procedure

The dissolution procedures are described under the section "Dissolution of Metals and Alloys". The following method was used in the analysis.

Dilute the sample, or aliquot thereof (Note 1, p. 7), to approximately 50 ml with water, and then, using a pH meter, adjust the pH of the solution to 4.5-5.0 using concentrated and 1:9 ammonia solution, as required. Add 5 ml of 50% sodium thiosulphate solution for samples of magnesium and aluminum metals and their alloys, or 10 ml for samples of brass and bronze, swirl to mix, and immediately adjust the pH to 6.5 \pm 0.1 using concentrated, 1:9 and 2:98 solutions of ammonia and/or hydrochloric acid as required. Transfer the sample solution to a 125-ml separatory funnel, dilute to approximately 100 ml with water, and proceed with the nickel extraction as described for the calibration curve.

Measure the absorbance of the whole sample, or aliquot thereof, taken for extraction, against a reagent blank that has been carried through the same procedure as the sample, and determine the nickel content by reference to the calibration curve.

Dissolution of Metals and Alloys

1. Brasses and Bronzes

The following procedure is recommended for samples containing 0.05% nickel or less and up to 1% tin.

Transfer a 0.5000 g sample to a 300-ml electrolytic beaker, cover, and add 25 ml of acid mix. When the reaction ceases, boil gently to remove oxides of nitrogen, cool, and dilute the solution to approximately 180 ml with water. (If the solution contains a small amount of black residue after dissolution with the acid mix, evaporate to fumes of sulphur trioxide, cool, add 2 ml of concentrated nitric acid, and dilute to 180 ml.) Remove the bulk of the copper and lead by electrolytic deposition on platinum gauze electrodes at 2 amp for 30 minutes, then add a 1 g ammonium sulphamate tablet to destroy nitrous oxides, and continue the

electrolysis for another 15 minutes. Evaporate the electrolyte until approximately 2 ml of sulphuric acid remain (Note 2, p. 7), cool, add 5 ml of 20% ammonium tartrate solution and a small amount of water, and heat gently until the solution is clear. Filter if lead sulphate is present, then determine the nickel as described under "General Procedure".

For samples containing 0.05% nickel or less and more than 1% tin, proceed as follows: Decompose the sample with 20 ml of 1:3 nitric acid solution, dilute to about 60 ml with water, and boil to precipitate tin as metastannic acid. Filter the hot solution through a #40 filter paper containing paper pulp into a 300-ml electrolytic beaker and wash the precipitate with hot 1% nitric acid solution. Transfer the paper and contents to a 250-ml beaker, cover, add 10 ml of concentrated perchloric acid and 20 ml of concentrated nitric acid, and evaporate slowly to fumes of perchloric acid to destroy the paper. Volatilize the tin (also arsenic and antimony, if present) as the bromide by successively treating the solution with 10-ml portions of hydrobromic acid and evaporating to perchloric acid fumes until the acid layer is no longer cloudy. Then evaporate the solution to dryness, take up the residue with 16 ml of 1:1 sulphuric acid, and combine this solution with the original filtrate. Dilute the resultant solution to 180 ml with water, remove copper and lead electrolytically, and then proceed with the nickel determination as described in the preceding paragraph.

For samples containing more than 0.05% nickel proceed as follows: Decompose the sample as described above for low tin samples, add 5 ml of ammonium tartrate solution, filter if lead sulphate is present, dilute to an appropriate volume depending on the expected nickel content of the sample, and determine the nickel using a suitable aliquot of this solution.

For silicon bronzes proceed as follows: Decompose the sample with 25 ml of acid mix in a 100-ml platinum dish, add approximately 20 drops of hydrofluoric acid, and evaporate the solution to fumes of sulphur trioxide. If the expected nickel content does not exceed 0.05% and less than 1% tin is present, transfer the solution to an electrolytic beaker (filter if lead sulphate is present), add 2 ml of concentrated nitric acid, dilute to 180 ml, remove copper electrolytically, and proceed as described above for low tin samples. If more than 1% tin is present, carefully evaporate the solution to complete dryness, take up the residue with 20 ml of 1:3 nitric acid solution, transfer to a 250-ml beaker, dilute to about 60 ml with water, and proceed as described above for high tin samples. If the expected nickel content is greater than 0.05%, continue as described in the preceding paragraph.

2. Magnesium Metal and Alloys

Transfer a 0.5000 g sample to a 250-ml beaker, add 35 ml of water, cover, and slowly add 5 ml of concentrated hydrochloric acid. When the reaction ceases, add 1 ml of concentrated nitric acid and boil gently to remove oxides of nitrogen. Cool, filter if necessary, add 5 ml of 20% ammonium tartrate solution (Note 3, p. 7), and determine the nickel as described under "General Procedure".

3. Aluminum Metal and Alloys

The following procedure is recommended for super-pure aluminum metal and aluminum alloys containing less than approximately 0.7% silicon.

Transfer a 0.5000 g sample to a 250-ml beaker, add 10 ml of water (or 10 ml of 0.05% iron solution for super-pure aluminum metal in order to hasten the dissolution process), cover, and add 5 ml of concentrated hydrochloric acid. When the reaction ceases, add 1 ml of concentrated nitric acid and boil gently to remove oxides of nitrogen. Cool, filter if necessary, then add 20 ml of 20% ammonium tartrate solution and determine the nickel as described under "General Procedure" (Note 4, p. 7).

For aluminum alloys containing more than 0.7% silicon proceed as follows: Decompose the sample as described in the preceding paragraph, then add 5 ml of 1:1 sulphuric acid solution and carefully evaporate to dryness to ensure insolubility of silica. Add 30 ml of water and 2 ml of 1:1 sulphuric acid to the residue, heat until the solution clears, then filter through #40 filter paper containing paper pulp into a 250-ml beaker. Wash the paper and its contents well with hot water, then transfer both to a 100-ml platinum dish. Burn off the paper at a low temperature, then ignite at 600°C for a few minutes. Cool the residue, add 5 ml of water, 2 ml of 1:1 sulphuric acid, approximately 10 drops of hydrofluoric acid, cover, and then add nitric acid dropwise (5 drops at a time) until all of the silicon is in solution. Evaporate the resulting solution to fumes of sulphur trioxide, cool, wash down the sides of the dish with water, and evaporate to complete dryness. Take up the residue with a small amount of water and 5 drops of 1:1 sulphuric acid solution and combine this solution with the original filtrate. Evaporate the resulting solution to approximately 20 ml if the sample contains 0.05% nickel or less, filter if necessary, add 20 ml of ammonium tartrate solution, and then determine the nickel as described above.

Notes

- 1) The sample, or aliquot thereof, taken for analysis should not contain more than approximately 100 μg of nickel.
- 2) Tin and manganese do not interfere in the proposed procedure but may partially precipitate as metastannic acid and manganese dioxide during evaporation of the electrolyte. However, all of the MnO_2 and up to approximately 5 mg of tin will redissolve when the solution is evaporated to fumes of sulphur trioxide. MnO_2 in the electrolyte may also be redissolved by the addition of a few drops of concentrated hydrochloric acid. If the solution should remain cloudy after addition of ammonium tartrate, add 1 ml of hydrochloric acid and heat gently until the solution clears.
- 3) More ammonium tartrate may be required to complex large amounts of aluminum, thorium, zirconium, rare earths, tin and iron in highly alloyed samples of magnesium.
- 4) During pH adjustment of the reagent blank, some ammonium tartrate may crystallize out of solution but will redissolve with the subsequent treatment and dilution with water.

EXPERIMENTAL

Effect of pH and Diverse Ions

Cobalt^{II}, copper^{II}, palladium^{II}, platinum^{II} and gold^{III} are known to form dimethylglyoxime complexes which, depending on experimental conditions, are extracted to a certain extent with chloroform (12). However, with the exception of copper, which is a principal constituent of brasses and bronzes, the possible interference effects of the remainder of these cations were not investigated in the present work because they do not normally occur as impurities or alloying elements in the materials under consideration. If cobalt should be present in the sample to be analysed, its dimethylglyoxime complex, which is only slightly extracted by chloroform (12), can easily be removed from the extract by shaking it with dilute ammonia solution, but sufficient dimethylglyoxime must be added prior to the extraction step to react with the cobalt and leave an excess for the nickel. Copper is a serious interferent in this method. The copper^{II}-dimethylglyoxime

complex imparts a brownish colouration to the chloroform phase (12), and yields high results for nickel. Consequently, large amounts of copper must either be removed from the sample solution or be suitably complexed to prevent reaction with dimethylglyoxime. Nielsch (5) showed that large amounts of copper can be effectively complexed with sodium thiosulphate; therefore, this technique was utilized in the present investigation.

Claassen and Bastings (13) have shown that the optimum pH range for the formation of a stable copper thiosulphate complex is 5.5-6.5. However, Cheng (14) states that instability of the complex occurs above pH = 7; tests carried out in this laboratory confirm this statement. Nielsch (5) recommends a pH of 6.5 for the extraction of nickel from solutions of copper complexed with sodium thiosulphate; consequently, this pH was also chosen for the present work.

On applying the method of Penner and Inman (11) to the determination of nickel in brasses and bronzes (with suitable modifications to include complexing of copper with sodium thiosulphate), difficulties associated with the precipitation of zinc hydroxide at approximately pH = 5.5 were encountered. However, it is known that sodium thiosulphate also forms a weak zinc complex (14), and the above difficulty was eliminated by adjusting the pH to 4.5-5.0 prior to the addition of thiosulphate and subsequent pH adjustment to 6.5. Tests showed that approximately 5 g of sodium thiosulphate were required to complex 250 mg of zinc. Therefore, because an excessive amount would be required to complex both copper and zinc, it was considered preferable, for samples of brass and bronze containing very small amounts of nickel, to remove the bulk of the copper electrolytically.

The literature contains several conflicting statements regarding the effect of manganese on the extraction of nickel^{II}-dimethylglyoximate with chloroform. Sandell (12) and Oelschläger (6) have reported that large quantities of manganese inhibit the extraction of nickel, presumably because of air-oxidation of manganese^{II} in ammoniacal solution, which, in turn, oxidizes the chloroform-soluble nickel^{II} complex to the chloroform-insoluble nickel^{IV} complex. Oelschläger also states that some manganese enters the chloroform phase and, to counteract these effects, he specifies extraction of the nickel complex from solutions containing hydroxylamine hydrochloride. Conversely, Claassen and Bastings (15) state that complete extraction of nickel can be obtained from citrate solutions at pH = 7.2-9.5 in the presence of as much as 25 mg of manganese. Because manganese is present in many brasses and bronzes and in magnesium and aluminum alloys, tests were carried out to determine the behaviour of manganese under the various experimental conditions recommended by the above workers.

Experiments were performed at pH \approx 8.5 with ammoniacal citrate solutions containing 50 mg of manganese^{II} and known amounts of nickel, and in the absence of the possible reducing action of sodium thiosulphate. After addition of dimethylglyoxime, these solutions were allowed to remain in contact with air for 15 minutes prior to the extraction and subsequent determination of nickel according to the procedure described previously. Complete recovery of the added nickel was obtained in these tests. Similarly, tests performed at pH \approx 6.5 and 8.5 with ammoniacal tartrate solutions, both with and without sodium thiosulphate, and after the solutions were allowed to stand in contact with air for 3 hours, showed that up to 100 mg of manganese^{II} did not interfere. Colorimetric determination of manganese in the extracts from the above tests indicated that essentially no manganese (or less than 5 μ g) was extracted into the chloroform phase. The results of these tests showed that manganese does not inhibit the extraction of the nickel complex from citrate and tartrate solutions at the pH values tested, and that nickel may be quantitatively extracted by the proposed procedure from solutions containing up to 100 mg of manganese^{II}.

The possible interference effects of various other ions that occur as impurities or alloying constituents in samples of brass, bronze, aluminum and magnesium metals and their alloys were tested separately by the proposed method on test solutions containing 50 μ g of nickel. The results of these tests (Table 1) showed that, for the quantity of each ion tested, none interfered in the nickel determination.

TABLE 1

Effect of Diverse Ions on the Determination
of Nickel by the Proposed Method

Nickel Taken, 50 μ g		Ni Found, μ g
Diverse Ion Taken, mg		
125 Th ^{IV}	[Th(NO ₃) ₄]	50.5
100 Zr ^{IV}	[ZrOCl ₂]	50.5
* 10 Pb ^{II}	[Pb metal decomposed with HNO ₃]	49.8
10 Si ^{IV}	[Na ₂ SiO ₃ ·9H ₂ O]	51.0
100 Sn ^{IV}	[Sn metal decomposed with HCl and HNO ₃]	50.0
100 Fe ^{III}	[Fe metal decomposed with HCl]	50.0
100 Li ^I	[Li ₂ SO ₄ ·H ₂ O]	50.5
* 100 Ag ^I	[AgNO ₃]	50.0
* 100 Cd ^{II}	[Cd metal decomposed with HNO ₃]	50.5
80 Rare Earths	[Mischmetall (Ce 50%, La 20%, others 30%) decomposed with HCl and HNO ₃]	51.0
5 Cr ^{III}	[CrK(SO ₄) ₂ ·12H ₂ O]	50.5

* Pb, Ag and Cd also form complexes with sodium thiosulphate (16).

Application to Brasses, Bronzes, Magnesium and Aluminum Metals
and Their Alloys

To determine the accuracy of the proposed method, it was applied to the determination of nickel in a number of National Bureau of Standards and British Chemical Standards samples of brass, bronze, and magnesium and aluminum alloys. In addition, because few magnesium and aluminum standard samples were available with nickel contents in the range 0-0.10%, a series of synthetic standards in which the added nickel varied from 0.001 to 0.10% was prepared and analysed by the proposed method. The results of these analyses are given in Tables 2, 3 and 4.

TABLE 2

The Determination of Nickel in N.B.S. and B.C.S.
Brass and Bronze Samples

Sample	Certified Value and Range % Nickel	Nickel Found (%)
NBS-1101 Cartridge Brass (wrought)	0.013 (0.013-0.014)	0.013, 0.014*
NBS-1102 Cartridge Brass (wrought)	0.005 (0.005-0.006)	0.0053, 0.0052*
NBS-1106 Naval Brass (composite) (0.74% Sn)	0.025 (0.024-0.025)	0.025, 0.025*
NBS-1108 Naval Brass (composite) (0.39% Sn)	0.033 (0.031-0.037)	0.032, 0.032*
NBS-1109 Red Brass (cast)	0.10 (0.10-0.12)	0.104, 0.104*
NBS-1110 Red Brass (composite)	0.053 (0.051-0.054)	0.052, 0.052*
NBS-37E Sheet Brass (1.00% Pb, 1.00% Sn)	0.53 (0.52-0.55)	0.534
NBS-52C Cast Bronze (7.85% Sn)	0.76 (0.76-0.77)	0.759
NBS-62D Manganese Bronze (1.23% Al, 0.66% Mn)	0.28 (0.27-0.29)	0.286
NBS-63C Phosphor Bronze Bearing Metal (9.35% Pb, 9.03% Sn, 0.52% Sb, 0.145% P)	0.32 (0.31-0.32)	0.312
NBS-124D Ounce Metal (5.20% Pb, 4.56% Sn)	0.99	0.998
NBS-158 Silicon Bronze (2.72% Si, 1.48% Fe, 1.31% Mn, 0.97% Sn, 0.54% Al)	0.006 (0.0056-0.0064)	0.0063
NBS-164 Manganese Aluminum Bronze (6.21% Al, 4.68% Mn, 2.52% Fe, 0.63% Sn)	0.046 (0.044-0.05)	0.046
NBS-184 Leaded Tin Bronze (6.38% Sn, 1.44% Pb)	0.50 (0.48-0.51)	0.509
BCS-183/1 Bronze (5.01% Sn, 3.51% Pb, 0.51% P, 0.24% Sb, 0.14% As)	0.51 (0.47-0.53)	0.503
BCS-207 Bronze "C" (9.80% Sn)	0.09 (0.08-0.11)	0.095
BCS-179 Manganese Brass "B" (1.03% Mn, 0.91% Fe, 1.62% Al, 1.75% Sn, 0.78% Pb)	1.01 (0.96-1.05)	1.00

* Nickel determined by the iodine-oxidation procedure.

TABLE 3

The Determination of Nickel in N.B.S. and B.C.S.
Magnesium and Aluminum Alloys

Sample	Certified Value and Range % Nickel	Nickel Found (%)
NBS-171 Magnesium-base Alloy (2.98% Al, 1.05% Zn, 0.45% Mn)	0.0009 (0.0007-0.0014)	0.0008
BCS-307 Cerium Zinc Zirconium Magnesium Alloy (2.84% Rare earths, 2.08% Zn, 0.56% Zr)	0.001 or less	0.0006
NBS-85B Aluminum Alloy (wrought) (3.99% Cu, 0.61% Mn, 0.18% Si)	0.084 (0.079-0.091)	0.089, 0.088*
NBS-86C Aluminum Alloy (casting) (7.92% Cu, 0.68% Si)	0.030 (0.02-0.035)	0.030, 0.030*
NBS-87a Silicon Aluminum Alloy (6.24% Si, 0.26% Mn)	0.57	0.561
BCS-182/1 Silicon Aluminum Alloy (11.48% Si, 0.28% Mn)	0.04 (0.03-0.05)	0.040
BCS-268 Silicon Aluminum Alloy (4.85% Si, 1.34% Cu, 0.22% Mn)	0.12 (0.11-0.136)	0.120

* Samples decomposed with hydrochloric and nitric acids; silicon filtered off and discarded.

TABLE 4

The Determination of Nickel in Synthetic
Magnesium and Aluminum Samples

Sample	Total % Ni Present	Ni Found, %
Mg + 0.0010% Ni	0.0012	0.0012
Mg + 0.0050% Ni	0.0052	0.0052
Mg + 0.0100% Ni	0.0102	0.0102
Mg + 0.0250% Ni	0.0252	0.0253
Mg + 0.0500% Ni	0.0502	0.0504
Mg + 0.1000% Ni	0.1002	0.1005
NBS-171 + 0.0100% Ni	0.0109	0.0109
BCS-307 + 0.0100% Ni	Approximately 0.0110	0.0105
<hr/>		
Al + 0.0010% Ni	0.0010	0.0010
Al + 0.0050% Ni	0.0050	0.0050
Al + 0.0100% Ni	0.0100	0.0098
Al + 0.0250% Ni	0.0250	0.0247
Al + 0.0500% Ni	0.0500	0.0498
Al + 0.1000% Ni	0.1000	0.0988
Al + 0.0100% Ni + 10% Cu	0.0100	0.0100

Duplicate determinations of nickel in the above Mg and Al metals by the proposed method gave average results of 0.0002% and none detected, respectively. Certificate values for NBS-171 and BCS-307 are 0.0009 and 0.001% or less, respectively.

DISCUSSION

Tables 2 and 3 show that the results obtained by the proposed method are in excellent agreement with the NBS and BCS certificate values for nickel in various types of brasses and bronzes (i.e., lead, silicon, aluminum, tin, manganese and phosphor bronzes and manganese brass), and in magnesium and aluminum alloys. Table 4 shows that the results obtained on synthetic magnesium and aluminum samples agree favourably with the total calculated percentage of nickel present in the range of values up to approximately 0.10%.

NBS samples 1101 to 1110 (Table 2) are spectrographic brass standards which were previously analysed for the National Bureau of Standards by the Mines Branch laboratories, employing the iodine-oxidation procedure (17) after removal of the bulk of the copper by electrolysis and the remainder by hydrogen sulphide precipitation. The results of these analyses are in excellent agreement with those obtained by the proposed method, but the proposed method is simpler and more direct than the oxidation method, and has the added advantage of non-interference from manganese.

In determining nickel in aluminum alloys containing large amounts of silicon, tests showed that the silicon cannot be filtered off and discarded if accurate results are desired. Results obtained on NBS sample 87a and BCS samples 182/1 and 268 (Table 3), using this method, were 0.544, 0.033 and 0.116 respectively, showing that small amounts of nickel were occluded and removed with the silicon. Table 3 shows that this negative error is insignificant for quantities of silicon up to approximately 0.7%.

The procedures presented in this report are suitable for samples containing between 0.0005 and 1% of nickel, but nickel contents below 0.0005% can be estimated fairly accurately since the reagent blank in all cases contains approximately 2 μ g or less of nickel. Magnesium metal and alloy samples generally contain only trace amounts of nickel, but samples of brass, bronze and aluminum alloys often contain more than 1% nickel and can be successfully analysed by reducing the initial sample weight. However, gravimetric analysis is considered superior for samples containing more than 1% of nickel, because of the high dilution factor involved. The sensitivity of the proposed method is high, the technique required is simple, and the results are reproducible under routine conditions.

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Authors' Note:

While the above manuscript was under editorial review, an abstract of a paper by C.M. Dozinel, entitled "Photometric Determination of Trace Amounts of Nickel in Copper and Its Alloys", was published in Analytical Abstracts 10, 2604 (1963); Chim.Anal. 44 (10), 436-438 (1962). The method described in this abstract is also based on spectrophotometric measurement of the chloroform extract of nickel^{II}-dimethylglyoximate.

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