

**COLOURIMETRIC DETECTION AND SEMIQUANTITATIVE
DETERMINATION OF NICKEL IN SOME ORGANIC
COMPOUNDS AND IN STEEL.**

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ABSTRACT

The nickel ion is liberated from some organonickel compounds and steel, through oxygen flask combustion and wet digestion in Kjeldahl flasks. The digested solution is spotted on silica gel thin layer plates and a mixture of acetone-concentrated HCl-acetylacetone (100+1+0.5) is used as solvent to separate nickel from associated elements. Ni spots are sprayed with an alcoholic dimethylglyoxime solution where the red spots are correlated with a premade colour index using known amounts of Ni.

A parallel determination is done by scratching the Ni spots, elution and measurement of the absorbance of the Ni-dimethylglyoxime complex at 445 nm.

Keywords Nickel, dimethylglyoxime, TLC separation, organonickel compounds, detection, semiquantitative detmn., steel.

A number of new ligands and chelating agents were used for the spectrophotometric determination of Ni on different scales. 2-Hydroxy-1-naphthaldoxime¹, 4-(2-thiazolylazo) resacetophenone

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oxime², 2-hydroxy-1-acetonaphthone oxime (2-HANO)³, hydroxy naphthol blue (HNB)⁴, 2-[2-(4-methylquinyl)azo]-5-diethylaminophenol⁵, 5-imino-1-phenyl-3-ethyl-2-imidazolidinone-4thione⁶, salicylaldehyde guanylhydrazone(SAG)⁷, 2-(5-bromo-2-thiazolylazo)-5-dimethyl-dimethyl-aminobenzoic acid⁸, 2-(4,5-dimethyl-thiazolylazo)-5-dimethyl-aminobenzoic acid⁹ quinoxalin-2,3-dithiol¹⁰, 1-(8-hydroxy-quinoline-7-azo)-p-nitrobenzene¹¹, 2-(2-imidazolylazo)phenol-4-sulfonic acid(R)¹², benzylamine-dimethylglyoxime¹³, bromo-PADAP 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol¹⁴, 2,6-dichloro-4-sulfamoylbenzenediazoaminoazobenzene¹⁵, 7-methyl-2-chloro-quinoline-3-carbaldehyde theiosemicarbazone (MT)¹⁶, 4-(2-quinolyl-methyleneamino)-1-phenyl-2,3-dimethyl-5-pyrazolone(QPP)¹⁷, and hexylthioglycolate(HTG)¹⁸.

Also, chromatographic methods^{19,20}, polarographic²¹, voltametric²², ionselective electrodes²³, potentiometric titration²⁴, and ICP-AES^{25,26} were developed. Ni was determined in steel by a variety of methods; high frequency inductively coupled plasma emission spectroscopy²⁷, a.c. oscillography²⁸, oscillographic titration²⁹ and spectrophotometric methods³⁰. Polyurethane foams loaded with dimethylglyoxime³¹ and dithizone³² have been used for the detection and semiquantitative determination of Ni and Ag, respectively.

The present work is carried out in an attempt to use dimethylglyoxime as spraying agent for sensitive and selective detection and semiquantitative determination of nickel (II) in digested solutions of its organic compounds and steel after separation on thin layer silicagel plates.

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EXPERIMENTAL

Reagents and materials

All reagents are of analytical grade unless otherwise specified.

Silica gel G. BDH Chemicals.

Dimethylglyoxime, 0.5% solution in 70% ethanol,

Potassium persulphate, 4% solution, freshly prepared,

Concentrated nitric acid, 65% Merck,

Acetone, concentrated HCl, acetylacetone, AR,

Standard samples: 0.1 M solutions of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$; $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$; $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$; $\text{MnSO}_4 \cdot \text{H}_2\text{O}$; $\text{Al}(\text{OOCCH}_3)_3$ and FeCl_3 .

Ammonia, sp. gr. 0.80 AR; H_2O_2 30% Merck.

Organonickel compounds samples: Nickelocene, Nickel acetylacetonate, Cyclopentadienyl nickel carbonyl dimer, Bis (salicylidene)ethylene diamine nickel hydrate, Bis (diphenylphosphino) ethane nickel (II) chloride, Bis (triphenylphosphine) nickel chloride and Tetraphenyl porphine nickel (II) are supplied by Aldrich; some aminoacidato complexes of Ni (II), are prepared as cited in Ref.33. Iron-containing organonickel compounds are prepared according to published^{34,35} methods. Steel samples are kindly provided by Metals Research and Development Centre, Tebbeen, Cairo.

Apparatus: Oxygen flask, 1000 ml, with Pt gauze as sample holder, Microanalytical balance, E. Mettler (M5), with 20 g maximum load and sensitivity ± 0.001 mg.

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Micro Kjeldahl flasks, 25 ml,
Kirschiner applicator 0.25 mm,
Chromatographic plates 20 × 10 × 0.25cm,
Jars, 10 × 25 × 20 cm,
Microsyringes, 10 µl,
Hot air blower; Spraying equipment; Centrifuge,
Scanning UV/VIS spectrophotometer UV 240, and 1-cm cells,
Schimadzu corporation, Kyoto, Japan.

Procedure

A) The decomposition procedure:

i- Organonickel compounds: Weigh accurately 30-40 mg of the Ni compound into the conventional³⁶L-shaped ashless filter paper. Mix thoroughly with ca.25 mg of finely powdered KNO₃. Fold the paper as usual³⁶ and fix in the Pt gauze sample holder. Charge the flask with 25 ml 1:1 HCl. Flush with O₂ for 1 min. at a moderate rate, and combust as usual³⁶. After combustion is completed, rinse the stopper and the Pt gauze into the flask and evaporate the contents of the later till near 5 ml. Add 5 ml of conc. HNO₃ and repeat the evaporation. Transfer quantitatively with water to 25 ml volumetric flask.

ii- Iron-containing organonickel compounds Weigh: accurately samples in the range 50-70 mg in 25 ml Kjeldahl flasks. Add 5 ml conc H₂SO₄ and digest as usual. cool and add 2 ml H₂O₂ and evaporate. Repeat the addition of H₂O₂ till the solution becomes clear. Let to cool, add 5 ml conc. HNO₃ and redigest. After complete cooling, transfer quantitatively to 25 ml volumetric flask.

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iii- Steel samples: In 25 ml Kjeldahl flask, weigh accurately 150-300 mg of the powdered alloy. Add 12 ml of aqua regia then boil and evaporate till near dryness. Let to cool, then cautiously add 2 ml H_2O_2 dropwise on the walls of the flask. Boil for 3 min., then add 7-10 ml conc. HNO_3 and boil. The addition of H_2O_2 can be repeated twice or more. The change to the nitrate form is shown by the change of the clear green solution to clear brown.

Digested solutions by the three procedures are ready for being chromatographed.

B) Separation on thin layer plates: Plates are prepared as detailed previously³⁷, then are activated at 110°C . An authentic mixture of Ni and associated ions is made by appropriate dilution of the 0.1 M stocks. A sample of 10 μl of the mixture is applied with a microsyringe at a distance of 3 cm from one edge of the plate. On the same plate apply a series of spots of each cation solution. Each spot is applied 2 cm apart. Develop the chromatogram using the recommended mobile phase, viz. a ternary mixture of 100 ml acetone, 1 ml conc. HCl and 0.5 ml acetylacetone which is that used³⁸ for the separation of $(\text{NH}_4)_2\text{S}$ group.

The sequence of migration distances of the ions is:

$\text{Fe} > \text{Zn} > \text{Co} > \text{Mn} > \text{Cr} > \text{Ni} > \text{Al}$. Thus Ni spots are separated near the baseline away from the rest cations. Expose the plate to NH_3 vapour for a min. and then spray with the alcoholic dimethylglyoxime solution.

A correlation colour index is made by applying, in the same manner, a series of the standard Ni solution, ranging from 0.005-0.05 mg, besides the decomposed samples on the same plate. The plate is developed and dried as above. Expose to NH_3 vapour and spray with the oxime solution. Match the red-coloured spots of the decomposed

samples with the appropriate coloured spot, thus obtaining the approximate concentration.

The elution-spectrophotometric method: Using a micro spatula, loosen the spot and transfer its silicagel powder quantitatively into 25-ml separating funnel. Extract the Ni content by adding 2 ml of the dimethylglyoxime solution and ammonia to pH 9-10; shake for half a min. with two portions of CHCl_3 . Wash the combined extracts by shaking with ammonia solution (1+50), then strip the Ni from the organic phase by shaking for 1 min. with 0.5 M HCl. Discard the Chloroform layer and receive the aqueous layer in 25-ml volumetric flask.

To the flask, add 2 ml dimethylglyoxime solution, 2 ml of persulphate solution and 5 ml of conc. ammonia in that order³⁹. Complete to the mark with water and measure the absorbance at 445 nm after 10 min. against a blank. Concentrations are obtained by reference to a preconstructed calibration curve using known amounts of Ni in the range 0.4-2.2 $\mu\text{g/ml}$.

Results and Discussion

The most important photometric reagents for determining nickel are dioximes which give specific and fairly sensitive methods. Although there exist more sensitive methods, e.g, those employing 1-(2-pyridylazo)-2-naphthol (PAN) and pyridine-2-aldehyde-2-quinolyl hydrazone (PAQH), the oxime methods are the most selective³⁹.

Although Ni can be determined spectrophotometrically as the Ni-dimethylglyoxime chelate compound, TLC test involving colour development is more sensitive than the ordinary spectrophotometric

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method⁴⁰. Another major advantage of TLC for residual analysis is that elaborate clean up procedures prior to analysis are often unnecessary. Also, while cobalt interferes with the normal spectrophotometric method employing dimethylglyoxime, here, Co has a migration distance on silica gel thin layers which separates it enough from Ni without any need of the conventional masking of Co with cyanide.

From one hand, organonickel compounds constitute an important constituents of many of the industrial products, especially those compounds that contain additional elements besides nickel. From the other hand, Ni is used in different ratios in a wide variety of alloys rendering them more resistant to corrosion. Stainless steel typically contains 12-15% Ni, high speed cutting steel and high tensile strength steel contain 0.4-1.8% Ni⁴¹. Thus, the present work has undertaken the sensitive detection of the Ni ion as the red dimethylglyoxime complex after liberation from its compounds and alloys.

The oxygen flask method has extensively used for the decomposition of organometallic compounds. The difficultly-soluble nickel oxides, produced after combustion of organo-nickel compounds, are rendered soluble by mixing the solid sample with potassium nitrate followed by absorption in 1:1 HCl.⁴² Trials to decompose iron-containing organic compounds using the oxygen flask method were unsuccessful; this may be attributed to some sort of alloy formation with the platinum gauze sample holder. The alternative use of the silica spiral as sample holder was not tried due to the use of semi micro weights of the samples necessary for work on thin layers. Thus, wet digestion in Kjeldahl flasks was used for their decomposition (Table 2).

The ease of observing the red colour of the reaction products on the thin layer plates enabled the detection of Ni ion. As little as 0.44 μ g/ml of Ni has successfully been detected. The detection limit of Ni by the spot test reaction using dimethylglyoxime is 1 μ g/ml.

The use of a colour index for the spots on the thin layer has led to the development of a semi quantitative method for the determination of the nickel ion; this is very useful in the cases where high accuracy is not needed. A parallel elution-spectrophotometric method was developed to evaluate the semiquantitative procedure. The later has a determination error of \pm 8-18%, which is considered reasonable for such kind of procedures.

Table 1, shows the results of the analysis of 11 organo-Ni compounds by both procedures. Table 2 presents the analysis of Fe-Ni compounds. Only formulae are illustrated without the corresponding names because the alter are too lengthy.

Table3, shows the analysis of two samples of steel alloys, after their dissolution in aqua regia as the appropriate solvent.

In all cases, the elution-spectrophotometric procedure shows more accurate results, as expected, than the semiquantitative one as proved by the standard deviation values calculated for a number of five experiments with each procedure.

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Table 1: Microdetermination of nickel in some organonickel compounds after oxygen flask combustion.

Compound & Formula	%				
	Calcd	Semiquan. M.		Elution Spectr M	
		Found*	S	Found*	S
Nickelocene $C_{10}N_{10}Ni$	31.08	33.57	0.37	29.16	0.31
Nickel acetylacetonate (hydrate) $C_{10}H_{14}NiO$	28.10	30.38	0.47	26.21	0.17
Cyclopentadienyl nickel carbonyl dimer $C_{12}H_{10}Ni_2O_2$	38.67	36.19	0.50	41.32	0.30
N, N-Bis (salicylidene) ethylene diamine nickel (II) hydrate $C_{16}H_{14}N_2NiO_2$	18.0	19.61	0.23	16.91	0.19
Bis (diphenylphosphino) ethane nickel (II) chloride $C_{26}H_{24}Cl_2NiP_2$	11.12	10.23	0.23	11.94	0.16
Bis (triphenylphosphino) nickel (II) chloride $C_{36}H_{30}Cl_2NiP_2$	8.97	9.78	0.49	8.35	0.11
Tetraphenyl porphine nickel (II) $C_{44}H_{28}N_4Ni$	8.74	8.14	0.13	9.39	0.08
Bisleucinato nickel $C_{12}H_{24}N_2NiO_4$	18.40	19.86	0.38	17.19	0.24
Bis (N-benzoylglycinato) nickel (II) $C_{18}H_{16}N_2NiO_6$	14.14	13.00	0.31	15.17	0.24
Palmityl leucinato nickel $C_{22}H_{42}NNiO_4$	13.21	12.23	0.33	14.17	0.21
Stearyl leucinato nickel $C_{24}H_{47}NNiO_4$	12.43	13.36	0.39	11.58	0.19

* Average of five determinations

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Table 2: Microdetermination of nickel in some iron-containing organonickel compounds after wet digestion.

Formula	Ni%				
	Calcd	Semiquant. method		Elution Spectroph M.	
		Found*	S	Found*	S
$C_{17}H_{19}FeNi_2O_3P$	24.69	22.98	0.50	23.06	0.25
$C_{24}H_{20}FeNi_2$	24.38	22.30	0.45	23.56	0.20
$C_{30}H_{20}Fe_2Ni_2O_6$	16.64	17.05	0.38	17.96	0.16
$C_{36}H_{38}Fe_2Ni_2O_6P_2$	13.69	12.41	0.30	12.57	0.24

* Average of five determinations.

s = Standard deviation.

Table 3: Microdetermination of nickel in some steel samples after digestion in aqua regia.

Type of steel (Expected Ni%)	weight taken mg	Semiquantitative m.			Elution-spectroph. m.		
		Recovery %	Found Ni %	Average (s)	Recovery %	Found Ni %	Average (s)
Stainless steel	198.07	110.0	13.25	12.26	107.5	12.09	12.40
	170.40	90.0	10.78		93.0	11.76	
12% Ni	168.83	112.0	13.45	(1.37)	108.0	12.96	(0.82)
	150.54	114.0	13.07		109.0	13.08	
	141.68	89.5	10.74		92.0	11.28	
High speed cutting steel	304.37	88.1	1.59	1.77	90.0	1.61	1.77
	301.26	90.7	1.63		92.0	1.66	
(1.8 % Ni)	297.80	89.0	1.60	(0.23)	91.0	1.98	(0.19)
	256.50	112.0	2.02		110.0	1.97	

S = Standard deviation.

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التقدير اللونى شبه الكمي لأيون النيكل فى بعض مركباته العضوية وفى سبائك الصلب

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تم تحرير ايون النيكل الثنائى فى مركباته العضوية الفلزية عن طريق الحرق فى قارورة الأوكسجين باستخدام شبكة البلاتين كحامل بعد خلطها بـ ٢٠ - ٢٥ مج من نترات البوتاسيوم واستخدام ١٠ سم^٣ من حمض الهيدروكلوريك ١:١ كمحلول إمتصاص. بقية المركبات الأخرى تحتوى على الحديد بجانب النيكل، تم هضمها فى ورق كلدال باستخدام مخلوط من حمض الكبريتيك و النيتريك المركزين ثم إضافة فوق أكسيد الهيدروجين و الغليان. بينما تم هضم عينات الصلب فى الماء الملكى (٢٠ مل) ثم إضافة حمض النيتريك المركز فى النهاية، وينقل بالماء إلى حجم ثابت.

يقدّر تركيز أيون النيكل فى جميع العينات عن طريق الفصل على طبقة السيليكا الرقيقة وإستخدام خليط من الأسيتون - حمض الهيدروكلوريك المركز - والأسيتل أسيتون بنسبة ١٠٠ : ١ : ٠,٥ كمذيب. يتم رش بقع أيون النيكل الموجودة فى قاع الطبقة قرب خط البداية برذاذ من المحلول الكحولى لثنائى ميثيل الجلايوكزيم (٠,٥%).

يتم مضاهاة البقع الحمراء الناتجة مع ألوان مجموعة من بقع النيكل ذات تركيزات معلومة ومعالجة بنفس الطريقة، حيث يتم تحديد التركيز التقريبي، فى نفس الوقت تم مقارنة الطريقة شبه الكمية بالقياس المباشر لتركيز النيكل فى البقعة عن طريق كشطها واستخلاص الأيون منها وتقديره طيفيا باستخدام ثنائى ميثيل الجلايوكزيم كدليل لوني وقياس الإمتصاص عند طول موجى قدره ٤٤٥ نانومتر فى المدى ٠,٤ - ٢ جزء فى المليون.