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ESTIMATION OF TRACES OF NICKEL IN SODIUM METAL

by

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Summary

A simple and sensitive method is described for the determination of traces of nickel in sodium metal. The nickel is complexed with potassium cyanide and the absorption measured spectrophotometrically at $268\text{ m}\mu$. Interference of iron and chromium is removed by precipitation of the hydroxides from homogeneous solution. This method should be applicable to a wide range of materials.

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CONTENTS

	Page
1. Introduction	1
2. Experimental	1
3. Study of Interferences	1
4. Procedure	3
5. References	3
Appendix	

1. INTRODUCTION

The dimethylglyoxime method, used extensively for the absorptiometric determination of traces of nickel (1), (2), (3), (4) suffers from many interferences (3). In addition the colour is unstable and must be measured soon after development. Most interferences may be removed by extraction of the nickel dimethylglyoxime complex with chloroform. It was found in this laboratory that the extraction procedure must be controlled very carefully to obtain reproducible results. Brummet and Hollweg (5), used 0.5% potassium cyanide solution to selectively dissolve nickel from oxidised films on nickel metal. The nickel complex was then determined spectrophotometrically at $268\text{ m}\mu$. This method appeared to be more suitable and was studied in order to determine whether it could be applied to the estimation of microgram quantities of nickel in metallic sodium.

2. EXPERIMENTAL

Optical densities were measured in 1 cm matched quartz cells with a Hilger 'Uvispek' spectrophotometer.

Reagents Standard Nickel Solution prepared from 'Analar' nickel sulphate heptahydrate. This salt was analysed by precipitation of the nickel as dimethylglyoxime and found to be 99.3% pure.

5% w/v Potassium Cyanide prepared from 'Analar' potassium cyanide. This chemical should have as low a ferrocyanide content as possible, and the solution should be freshly prepared every few days.

All other reagents used were of A.R. quality.

Preparation of Standard Curve.

The required aliquot of the standard nickel solution was measured from a micro burette into a 25 ml volumetric flask. 5% potassium cyanide (2.5 ml) was added and the mixture diluted to volume. The absorbance was measured at $268\text{ m}\mu$ with 0.8 mm slit width.

Figure 1 shows the method to be very sensitive. Beer's Law is obeyed to nickel concentrations of at least $2.4\text{ }\mu\text{g/ml}$. The solutions were found to be stable for at least two days, and unaffected by variations in the cyanide content from 0.1 to 0.5%. The concentration of 0.5% was adopted, however, since the interferences of copper and chromium appeared less pronounced in the stronger solution.

3. STUDY OF INTERFERENCES

The procedure given above was used in the presence of some common cations, (Table I). In addition, the following metals gave precipitates in 0.5% KCN:— Fe (III), Fe(II), Be, Pb, Sn, Zn, Mn, Zr, U.

Of the common anions, only ferrocyanide was found to interfere.

TABLE I
INTERFERENCE OF SOME CATIONS

Addition per ml	Nickel equivalent $\mu\text{g/ml}$
50 mg Na	0.00
2 mg Ca	0.00
50 mg NH_4	0.00
2 mg Ag	0.03
5 mg Al	0.00
5 mg Ce (IV)	0.02
5 mg Cd	0.00
100 μg Fe (III) tartrate	0.56
10 μg Cu (II)	0.40
10 μg Cu (I)	0.19
3 μg Co	1.73
5 μg Mo (VI)	0.73
1 μg Cr (VI)	0.22
5 μg Cr (III)	0.10

The interference of iron, chromium and copper was studied in detail, since these elements, particularly iron and chromium, are likely to be encountered in the analysis of sodium from stainless steel loops.

Removal of Iron

Rapid precipitation of iron with ammonium hydroxide was found to cause severe losses of nickel, probably by adsorption on the voluminous precipitate. If the precipitation is carefully controlled (9), by very slow addition of ammonia, the losses are greatly reduced. A double precipitation in this manner ensures complete recovery of the nickel. Double precipitation may be avoided, however, by separation of the ferric hydroxide by homogeneous precipitation (6) with urea, (Table II).

TABLE II
PRECIPITATION OF IRON

Method of Precipitation of Iron (0.5mg)	Ni taken (μg)	Ni found (μg)
Rapid precipitation with ammonia	1.00	1.10
Slow single precipitation with ammonia	1.00	0.96
Slow double precipitation with ammonia	1.00	1.01
Single precipitation with urea	1.00	1.00

Removal of Chromium

As shown in Table I, chromate ion absorbs strongly at $268\text{ m}\mu$ ⁸. If however, chromate is reduced to chromic ion the interference is decreased considerably. Any chromate originally present will be reduced by alcohol in the preparation of the sample. Chromium (III) will be removed with iron in the urea precipitation.

Removal of Copper

The cupricyanide complex absorbs weakly at $268\text{ m}\mu$ (Table I). This absorbance may be further decreased by 50% by reduction with hydroxylamine hydrochloride.

4. PROCEDURE FOR THE DETERMINATION OF NICKEL IN SODIUM IN THE PRESENCE OF IRON, CHROMIUM AND COPPER

1. Solution of the Sample

Dissolve a weighed amount of the sodium sample in absolute ethyl alcohol. Small amounts of water may be cautiously added to accelerate solution. Add concentrated hydrochloric acid to the sodium alcoholate until neutral, then 5mls in excess. Evaporate on a water bath to dryness. Bake in an air oven for two hours at 120°C . Dissolve the residue in the minimum amount of hot 0.1N hydrochloric acid, transfer to a volumetric flask, and make up to volume when cool.

2. Determination

Dilute an aliquot containing 5 to $75\text{ }\mu\text{g}$ of nickel to approximately 10 mls with distilled water. Add one drop of concentrated nitric acid and boil for a few minutes to oxidise iron. Add 0.5g of ammonium chloride and 0.5g of urea. Boil the solution gently until the pH has risen to 6 - 7, as tested by universal indicator paper. Simmer gently for a further 15 minutes to complete precipitation of chromium. Filter through a 4.5 cm No. 1 Whatman paper, and wash four times with 1 ml portions of hot 1% ammonium chloride. Add 5 drops of 10% hydroxylamine hydrochloride to the filtrate and boil gently for a few minutes. Add 2.5 mls of 5% potassium cyanide to the cold solution and dilute to 25 mls with distilled water.

Compare at $268\text{ m}\mu$ against a standard nickel solution treated in the same manner, and using 0.5% potassium cyanide solution containing hydroxylamine hydrochloride as a reference solution.

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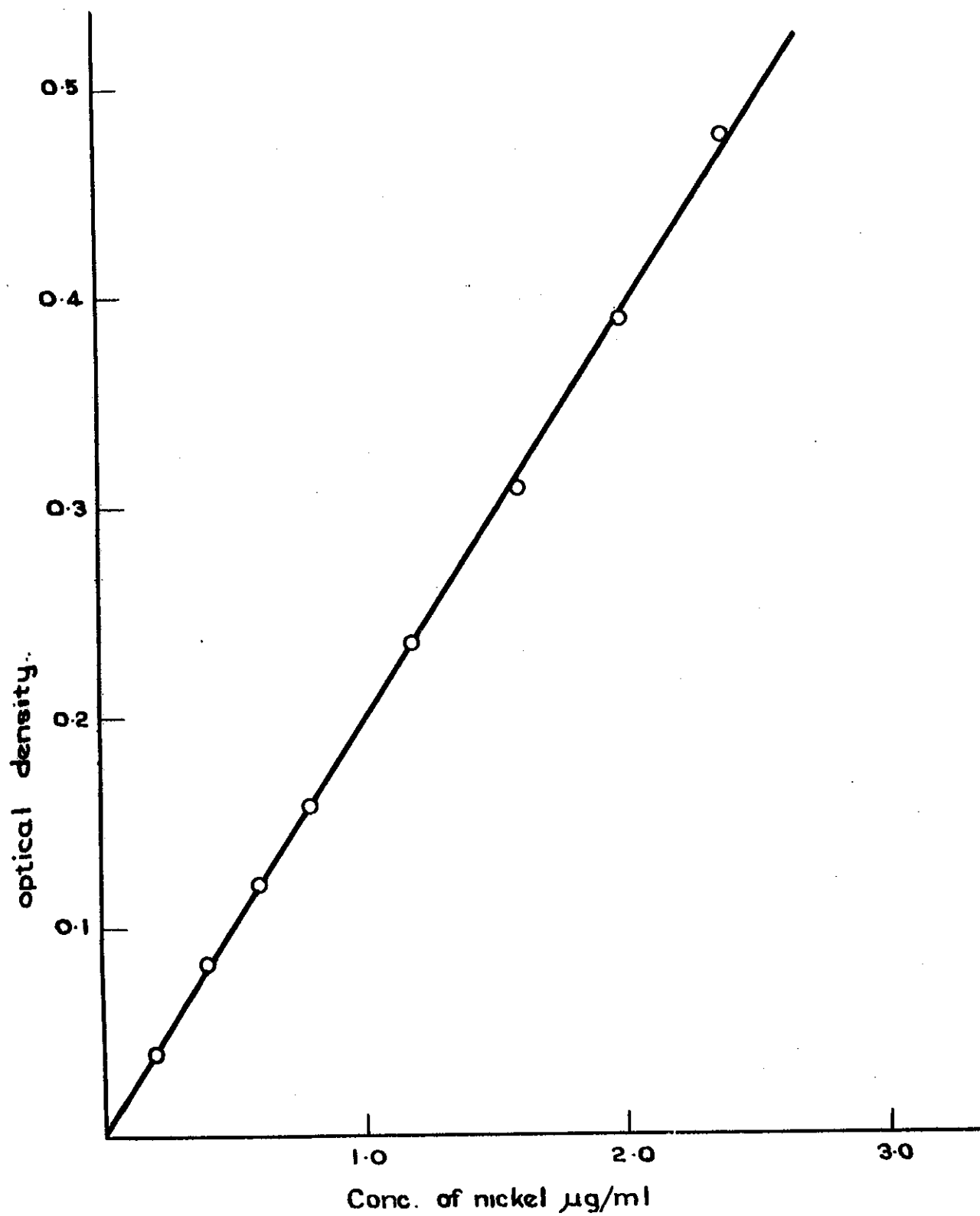


Fig.1. Determination of nickel by the
cyanide method.

