

Methods for the Determination of Trace Impurities in Nickel: Boron, Chloride, Sulfide and Sulfate

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Abstract

A method for the analysis of microgram quantities of chloride and sulfate in nickel and nickel nitrate is given. The reliability of the method has been shown by a quantitative recovery of added chloride and sulfate from a solution of nickel nitrate. The method is being applied for the determination of these impurities in electrodeposited nickel. Methods are also given for the determination of boron and sulfide, found as impurities, in the electrodeposited nickel.

On the basis of a very limited qualitative results¹⁻⁵), it has been suggested that a study of the impurity contents of electrodeposited nickel might throw some light on the processes taking place at the electrode during deposition. In spite of the obvious importance of the information that such quantitative data would provide, the analytical difficulties inherent to the problem apparently deterred workers from undertaking to solve it. In an attempt to study the extent of anionic contamination in electrodeposited nickel, attention was first devoted to the development of a method of analysis for a range of impurity content which preliminary studies quickly showed to be far too low for the conventional gravimetric and volumetric methods.

The method of CHIRNSIDE et al for the determination of boron in nickel was first extended to chloride analysis⁶). The chloride was finally estimated

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⁴) O. SCHAUS, Ph. D. Thesis, McHill University (1954).

⁵) V. ZENTER, A. BRENNER and C. W. JENNINGS, *Plating* **39**, 865 (1952).

⁶) T. SEKINE, H. GESSER, Z. NOSYK and Ed. JANZEN, *J. Electrochem. Soc. Japan* **29**, E 210 (1961).

by microdiffusion method⁷). Though reasonably good results were obtained, the method was time consuming and at times erroneous. The method could not easily include the analysis for sulfate which was also present. For a wide range of samples to be analysed, a more suitable method was sought to overcome these difficulties.

Recently various salts of chloranilic acid have found much use⁸⁻¹⁴) in analysis. In the present study, mercuric and barium chloranilates were used for the analysis of chloride and sulfate respectively. On account of the reaction between nickel and chloranilate ions, the interference of nickel ions was removed by ion exchange, prior to the determination of chloride and sulfate.

Experimental

By passing a 200 ml of aqueous solution containing upto 0.2 gm of Ni⁺⁺ in the form of nitrate together with the impurities through a column containing Amberlite IR 120 (20-50 mesh) in the hydrogen form, the interference of Ni⁺⁺ ions is effectively removed. The column is washed, the effluent is collected, neutralised and concentrated. The analysis of chloride and sulfate is carried out in two separate portions of the effluent.

Chloride and sulfate analysis

The methods followed are the same as described in⁸⁻¹⁰). In the calibration curve, prepared from standard ammonium salts, p.p.m. of Cl⁻ corresponds to 25.25 A (up to 30 p.p.m. of Cl) and p.p.m. of SO₄⁻ to 132.2 A (up to 60 p.p.m. of SO₄⁻) where A represents the absorbance of clear colored solution at 530 mμ in a 5 cm cell (Coleman Universal Spectrophotometer Model 14) against the reagent blank.

It was observed in separate experiments that large amounts of ammonium ions, produced in the neutralization of the effluent, increased the optical density. A correction was therefore necessary which amounted to 0.018% for Cl⁻ and 0.067% for SO₄⁻.

Results and Discussion

The concentration of chloride and sulfate in reagent grade (Fisher Certified Reagent) nickel nitrate was determined and found to be consistent with the manufacturers specifications. To test the homogeneity of the solid sample as well the quantitative recovery of both chloride and sulfate, a

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standard solution of nickel nitrate was prepared and to the various volumes of this solution fixed quantities of chloride and sulfate were added. The results showed that excess concentrations (Due to amounts present in nickel nitrate plus due to the interference of ammonium nitrate) of chloride and sulfate corresponded to $0.0238 \pm 0.0021\%$ and $0.0712 \pm 0.0028\%$ respectively. The following table gives the recovery of chloride and sulfate.

Table 1

Recovery of Chloride and Sulfate from Nickel Nitrate Solution 100 ml Solution contained 0.4952 gm of Nickel Nitrate 118 μgm Cl and 353 μgm SO_4 as excess amounts

Cl added μgm	SO_4 added μgm	Cl analysed μgm	SO_4 analysed μgm	Cl % Recovered	SO_4 Recovered
200	500	344	870	108.2	102.1
400	500	520	830	100.3	97.3
600	500	700	852	97.5	99.9
800	500	940	930	102.4	109.0
200	500	332	868	104.4	101.8
200	600	332	960	104.4	100.7
200	700	336	1030	105.7	97.8
200	1000	338	1404	106.3	103.7
Average				103.5	101.5
Standard Deviation				3.5	3.7

The analysis of chloride and sulfate in metallic nickel first required the slow dissolution of the sample in (1:3) nitric acid and then evaporating it to dryness at low temperatures to expell free acid. In doing so sulfide if present was oxidised to sulfate and passed into the solution. The determined amounts of sulfate thus included sulfate and sulfide. To determine sulfide, a fresh sample of the metal had to be dissolved in dilute hydrochloric acid, whereby, sulfide was lost and the analysis yielded only the amounts of sulfate. The difference between the two values gave the amount of sulfide.

Barium chloranilate method¹⁴⁾ could not be applied for the estimation of boron in nickel on account on the interference of sulfate ions. Boron was determined by solvent extraction method of PASZTOR¹⁵⁾. Chloride and nitrate solutions were found unsuitable. Nickel which did not dissolve in sulfuric acid was dissolved in a mixture of sulfuric acid and hydrogen peroxide. The excess of hydrogen peroxide was decomposed by heating. The detailed analysis results have been published elsewhere¹⁶⁾.

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¹⁶⁾ R. D. SRIVASTAVA and H. GESSER, Electrochimica Acta **9**, 1405 (1964).

The method of analysis for chloride and sulfate has been used to obtain the percentages of these in a variety of reagent grade metallic nitrates. After making appropriate corrections for the interference of produced ammonium ions, it was found that chloride results were in good agreement. The sulfate results were three to five times higher. The higher results for sulfate may be due to the interference of other ions present in the salts (S^- or PO_4^-) which are likely to interfere more in moderately acidic medium used for sulfate analysis than in strongly acidic medium used for chloride analysis.

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