

Zusammenfassung

Es wird ein volumetrisches Verfahren zur Bestimmung von Rhodanid mit Quecksilber(II)-nitratmaßlösung gegen Variaminblau als Redox-indicator angegeben. Auch Quecksilber(II)-ionen können bestimmt werden, wenn man mit einem Überschuß an Rhodanid versetzt und mit der Maßlösung zurücktitriert. Die Methode liefert genaue und wenig streuende Resultate.

Summary

Thiocyanate can be determined by titration with mercuric nitrate standard solution using Variamine blue as redox indicator. The determination of mercuric ions is possible by adding an excess of thiocyanate and back titrating with the standard solution. Results are exact and deviations are small.

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Amperometric Iodimetric Determination of Nickel(II) at Constant Voltage with Two Polarised Electrodes

By

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With 1 Figure in the Text

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It is well desired to develop a sensitive, rapid and accurate titrimetric method for the determination of trace amounts of nickel. Various methods developed for its estimation are time consuming and cumbersome. SUCHY¹⁴ precipitated nickel from its aqueous solution and titrated amperometrically with ammonium thiocyanate in pyridine, PEŠKOVÁ and GALLAI¹¹ estimated nickel with dioximes. Nickel has been quantitatively analysed by ŽDANOV and CEITLIN¹⁶ using 0.17 M sodium anthranilate at pH 5.4. LEVITMAN¹⁰ titrated a solution containing copper and nickel with rubeanic acid in ethyl alcohol by amperometric method. An alcoholic solution of dimethylglyoxime yields a sparingly soluble carmine precipitate with nickel in ammoniacal medium; at pH above 5, divalent

nickel precipitates quantitatively and has been determined by different methods^{1-4,6,7,9,12}. Nickel(II), involving this precipitation reaction, is separated from all elements other than Pt^{II}, Pd^{II} and Bi^{III}.

In the present investigations, the amperometric method at a constant voltage with two polarised electrodes has been applied with success for the determination of divalent nickel by iodine solution in presence of alcoholic dimethylglyoxime (DMG) solution in ammoniacal medium. DMG, combining firmly both with tetravalent as well as divalent nickel in this medium, lowers the redox potential where nickel(II) can be titrated with iodine solution, as oxidant, yielding a soluble wine-red compound when trace amounts of the elements is present. The coloration is stable for several days.

Experimental and Results

Nickel chloride used was analytical reagent grade and its stock solution has been standardised titrimetrically with standard potassium cyanide solution using silver iodide as the indicator⁸, and also iodometrically^{5,15}. *Sodium thiosulphate and iodine* used for the preparation of stock solutions were Merck's extrapure quality. The thiosulphate solution was standardised iodometrically against standard potassium dichromate (AnalR) solution every day before use. Iodine solution was prepared by dissolving 1.2656 g of iodine and 4.0 g of potassium iodide in air-free water in a 100 ml volumetric flask, and was standardised with a standard thiosulphate solution. One percent *DMG* solution was prepared in 99.0 percent ethyl alcohol, and all other solutions were prepared in conductivity water. The test solutions and standard iodine solutions were obtained by appropriate and accurate dilution of the concentrated stock solutions. All other chemicals used were reagent grade.

The experimental procedure for the amperometric titrations were essentially the same as described earlier¹³. Two platinum electrodes were immersed into the titration cell, and a constant voltage of 30 millivolt was applied to these electrodes. The titration mixture, usually 25 ml, was taken into the cell; it contained the test solution with excess DMG in an ammoniacal medium at pH 6.2 to 6.5. Titrant was added from a 2 ml semimicroburette with 0.01 ml divisions. The solution was stirred uniformly during titration with a magnetic stirrer. Current through the cell was measured with a sensitive galvanometer with lamp and scale arrangement and

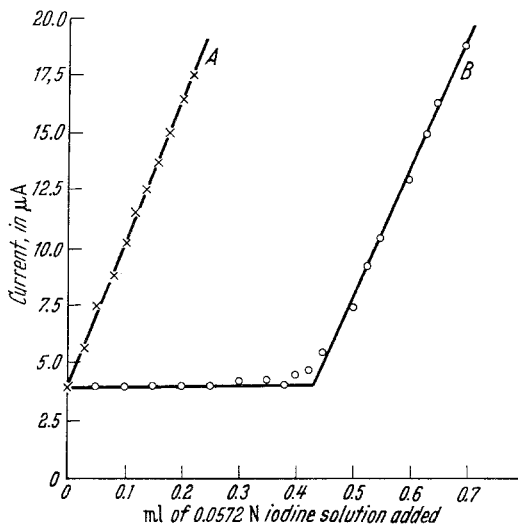


Fig. 1. A Blank experiment; B Amperometric titration of 0.7218 mg Ni²⁺ in excess alcoholic DMG, and ammoniacal medium with two polarised electrodes

two variable resistances, one in series and the other in parallel for critical damping. It was shunted in order to obtain a full scale deflection corresponding to a current of 20.0 μ A. Readings were noted one minute after each addition of the titrant.

The equivalence point was determined graphically by the usual plot of current in microamperes versus the volume of titrant added. The end

Table. *Amperometric Iodimetric Determination of Nickel(II) with Two Polarised Electrodes.*

Volume of titration mixture = 25 ml; Medium: ammonical + excess alcoholic DMG, with acetate buffer p_H 6.2 to 6.5

Determinations made	Amount of Ni ^{II} , in mg		Experimental error, %	
	taken	found	average	maximum
4	14.670	14.670	-0.23	-0.46
5	5.875	5.875	\pm 0.00	\pm 0.00
4	2.048	2.055	+0.42	+0.56
4	1.444	1.441	-0.34	-0.65
5	0.7218	0.7234	+0.36	+0.62
6	0.2937	0.2927	-0.44	-0.96
5	0.1465	0.1472	+0.75	+1.30
6	0.0584	0.0594	+3.25	+4.96

point of a titration corresponds to the volume of titrating reagent at the intersection of the excess reagent line with the line representing the preequivalence current as measured in air-free solution during the course of titration. Fig. 1B shows an example of the titration curve. End points are quite reproducible, and test solutions containing the same amount of element were titrated repeatedly several times for good and satisfactory results. The summarised results of these titrations are recorded in the table.

Discussion

Nickel(II) cannot be titrated by an oxidant, since it is a too weak reductant, (Ni^{2+}/Ni^{4+} , $E_0 = -1.78$ Volt). The formation of complexes affects the redox properties of the systems. In presence of dimethylglyoxime and an oxidant (iodine) nickel yields in ammoniacal medium a sparingly soluble wine-red compound, and the redox potential of the system is lowered so as under these conditions, nickelous ions have been successfully titrated with iodine using two indicator electrodes at 30 mV. The potential of system (I^3-/I^- , $E_0 = 0.53$) is independent of p_H upto 9.0. Thus iodine becomes a strong oxidant in neutral and alkaline solution, compared with many oxidising reagents, since the potentials of the majority of systems decrease as p_H increases.

The substances involved in the titration are not soluble, nickelous and nickelic dimethylglyoximes are sparingly soluble, but the oxidation of Ni^{2+} to Ni^{4+} at p_H 6.5 by iodine, is quantitative, corresponding to the stoichiometric reaction. The couple $[NiDMG]/[Ni(DMG)_2]$ behaves as irreversible, and the couple, triiodide-iodide is reversible; thus, the current is very low before the equivalence point, and rapid increase

in current indicates the end-point of the titration. The corresponding titration curve has the shape shown in Fig. 1B.

A review of the results in the Table shows that the substances, which are readily oxidised by iodine can be titrated in microquantities. Results are good, satisfactory and accurate upto very low concentrations, as low as 10^{-4} M. At lower concentrations, the error exceeds ± 5.0 percent. The method is rapid, simple and sensitive. The sensitivity frequently exceeds that of other methods, such as colorimetry and conductimetry. It has the advantage that it allows the determination of trace amounts of nickel, and is probably the best method for the accurate determination of traces.

Summary

The amperometric iodometric determination of nickel(II) in presence of excess dimethylglyoxime in ammoniacal medium at p_H 6.5, has been carried out at 30 millivolts with two polarised electrodes. The redox reaction is quantitative and the results obtained are accurate and satisfactory. The formation of complexes alters the oxidation potential of Ni^{2+}/Ni^{4+} to a lower value, so as the former is titrable with iodine. The method is simple, sensitive and convenient; and has the advantage that it permits determination of trace amounts of nickel of the order of 10^{-4} M with fair degree of accuracy. At higher dilutions, error exceeds 5 percent.

Zusammenfassung

Die amperometrische jodometrische Bestimmung von Nickel(II) wurde in Gegenwart von überschüssigem Dimethylglyoxim in ammoniakalischem Medium (p_H 6,5) bei 30 mV mit zwei polarisierten Elektroden durchgeführt. Die Redoxreaktion verläuft quantitativ und liefert genaue Ergebnisse. Durch die Komplexbildung mit Dimethylglyoxim wird das Redoxpotential Ni^{2+}/Ni^{4+} erniedrigt und dadurch die jodometrische Titration des Ni^{2+} ermöglicht. Das Verfahren ist empfindlich, einfach und bequem und hat den Vorteil, daß auch Spuren (10^{-4} m) mit guter Genauigkeit bestimmt werden können. Bei größeren Verdünnungen beträgt der Fehler mehr als 5%.

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Zur komplexometrischen Titration von Wismut

Teil I

Indicatoren

Von

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Mit 13 Textabbildungen

(Eingegangen am 2. Dezember 1961)

Die vorliegende Arbeit entstand aus der Notwendigkeit heraus, Wismutgehalte in verschiedenen Oxiden¹² genau und schnell zu analysieren. Dafür bot sich die komplexometrische Titration als einfache und sichere Methode an. Nach Angaben in der Literatur^{10,19,23,25,27-29} ist Brenzcatechinviolett als Metallfarbindicator für chelatometrische Wismutbestimmungen geeignet.

Wir haben den optimalen p_H -Wert für den Indicatorumschlag sowie die Genauigkeit der Titrationsmethode an Brenzcatechinviolett als Standardindicator untersucht. Weitere Indicatoren, die in der Literatur beschrieben werden, haben wir auf ihren Farbumschlag geprüft, ihre Absorptionsspektren ermittelt und auf ihre praktische Verwendbarkeit hin untersucht.

Nach der Einstellung von salpetersauren Wismutlösungen auf einen bestimmten p_H -Wert mit verdünntem Ammoniak^{23,25,27} traten wiederholt Fehlbestimmungen an Wismut auf, die auf der Bildung von Hydrolyseprodukten (Polykationen und schwerlösliche Wismutylverbindungen) beruhen¹³. In dem nachfolgenden Teil 2 dieser Arbeit werden die Bedingungen näher untersucht, die zur Bildung dieser Produkte führen. Es werden Methoden angegeben, um Fehlbestimmungen zu vermeiden.