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Mendeleev Commun., 2004, 14(5), 223–225
Mendeleev Communications

Determination of nickel(II) by its influence on the oxidation of 3,3′,5,5′-tetramethylbenzidine with periodate

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DOI: 10.1070/MC2004v014n05ABEH001863

The negative catalytic action of nickel(II) in the oxidation of 3,3′,5,5′-tetramethylbenzidine with periodate and its positive catalytic effect in the same reaction in the presence of an activator (dimethylglyoxime) have been applied to the development of analytical procedures for the determination of this metal ion, which proved to be more sensitive in the case of a positive catalytic effect (the detection limit of nickel is 10^3 times lower).

Nickel is a trace element that is necessary for plants, animals and humans, being a constituent of urease. At the same time, nickel is toxic within a certain concentration range. Thus, in natural water in concentrations higher than 0.1 μg ml^{-1}, nickel is hazardous for aquatic organisms and irrigated plants. Nickel may cause allergic reactions in humans, and nickel compounds are carcinogenic.[1] For the development of simple and sensitive analytical procedures for the determination of nickel, catalytic methods of analysis have been successfully used. However, nickel is a metal for which catalytic action is not typical, and only a few techniques for its determination by catalytic methods have been published.[2–13] The most sensitive procedures for the catalytic determination of nickel have been proposed recently.[8–11] The negative catalytic action of nickel has also been used for its determination, though the sensitivity in this case is not so high.[12,13]

The purpose of this study involves the analytical applications of the both types of nickel catalysis that we have observed.

Distilled water additionally purified on a Millipore water purification system was used in the experiments. Commercial 3,3′,5,5′-tetramethylbenzidine (TMB) from Riedel de Haën (Germany), dimethylglyoxime (DMG) from Reakhim (Russia) and sodium periodate from Reanal A.R. (Hungary) were used. An ethanolic solution of TMB (2.5×10^{-2} mol dm^{-3}) and an aqueous solution of $NaIO_4$ (usually, 4.3×10^{-2} mol dm^{-3}) were prepared by dissolving weighed portions of the compounds. A stock nickel(II) solution containing 1 mg dm^{-3} was prepared from $NiCl_2\cdot6H_2O$ and acidified by sulfuric acid to pH 1.8–1.9. Solutions with lower nickel contents were prepared by dilution with water. Borate buffer solutions were used. A KFK-3 spectrophotometer (ZOMZ, Russia) was used for the absorbance measurements. The absorption spectra of the products of TMB oxidation with periodate were recorded on Shimadzu (Japan) and KFK-3 spectrophotometers.

Procedure for the determination of nickel(II). The reagents were placed in a 10 ml test tube in the following sequence: 3.9 ml of a borate buffer (pH 6.8); 0.5 ml of a nickel(II) solution (concentration of 1×10^{-3}–1 μg ml^{-1}) or 0.5 ml of water in a blank experiment; 0.05 ml of 1.25×10^{-2} mol dm^{-3} TMB; 0.05 ml of 8.5×10^{-2} mol dm^{-3} DMG or 0.05 ml of ethanol in the case of the reaction without DMG; 0.5 ml of 2.15×10^{-3} mol dm^{-3} $NaIO_4$. The total volume of the reaction mixture was 5 ml. As it has been found before, this order is the most efficient to ensure the highest possible rate of the reaction. The addition of periodate was taken as the time of reaction start. The reaction mixture was stirred and then transferred into a spectrophotometer cell (l = 1 cm). In 1 min, the absorbance of TMB oxidation products at 650 nm (A_1) was measured against water. In order to obtain positive analytical signals, it was calculated as the absolute value of the difference in the absorbances of uncatalysed and catalytic reactions: $\Delta A_1 = |A_{\text{without Ni(II)}} - A_{\text{Ni(II)}}|$.

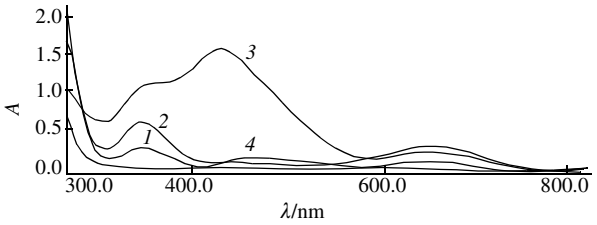

Figure 1 Absorption spectra in the 3,3′,5,5′-tetramethylbenzidine (TMB)–$NaIO_4$ system recorded 20 min after the reaction started (borate buffer, pH 6.8; 2.15×10^{-4} mol dm^{-3} $NaIO_4$; 1.25×10^{-4} mol dm^{-3} TMB): (*1*) 1×10^{-2} μg cm^{-3} of nickel and no dimethylglyoxime (DMG); (*2*) without either nickel or DMG; (*3*) 1×10^{-2} μg cm^{-3} (1.7×10^{-6} mol dm^{-3}) of nickel and 1.7×10^{-4} mol dm^{-3} of dimethylglyoxime; (4) nickel(II) bis(dimethylglyoximate) (1.7×10^{-6} mol dm^{-3}).

Choice of the indicator system. For the determination of nickel, the oxidation of TMB with periodate was used. This reaction is convenient because TMB and its solutions are stable in air and nontoxic (in contrast to other aromatic amines), and the intermediate product of oxidation of TMB with periodate has an intense bluish green colour suitable for visual detection. As a result of the oxidation of TMB with periodate in the range

Table 1 Analytical characteristics of the determination procedure for nickel(II) with the use of a TMB–$NaIO_4$ reaction.

Procedure	Linear range/ μg cm^{-3}	Calibration curve parameters[a]					RSD	C_{min}/μg cm^{-3}
		a	s_a	b	s_b	r		
Without DMG	0.5–3.0	0.029	0.02	0.155	0.01	0.991	0.06 (1 μg cm^{-3} Ni)	0.3
With DMG	3×10^{-4}–3×10^{-3}	0.039	0.01	50	6	0.987	0.02 (5×10^{-4} μg cm^{-3} Ni)	1×10^{-4}

[a] $Y = a + bX$, where $X = C_{\text{Ni}^{II}}$/μg cm^{-3}, and $Y = \Delta A_1 = |A_{\text{without Ni}^{II}} - A_{\text{Ni}^{II}}|$, measured 1 min after the start of the reaction.

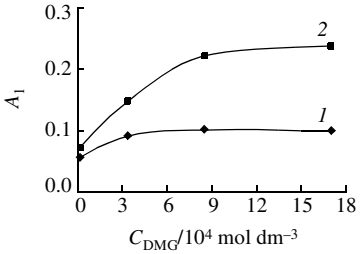

Figure 2 Dependence of the rate of the TMB–DMG–Ni^{II}–$NaIO_4$ reaction on the concentration of DMG (borate buffer, pH 6.8; 2.2×10^{-4} mol dm^{-3} $NaIO_4$, 1.3×10^{-4} mol dm^{-3} TMB): (*1*) without nickel; (*2*) 1 μg cm^{-3} of nickel.

pH 6–7, an intensely coloured blue-green product is formed, which exhibits two absorption bands at 370 and 650 nm. On deeper oxidation (for reaction time over 5–6 min if the periodate concentration does not exceed 4.3×10^{-3} mol dm^{-3} and even faster for higher concentrations of the oxidant), it transforms into an orange product (absorbance maximum at 450 nm).[14] In this study, the indicator reaction in the presence of nickel was monitored by measuring the concentration of the above (blue-green) product at 650 nm.

The negative catalytic effect of nickel ions in the TMB–$NaIO_4$ reaction was uncovered while studying the catalytic action of manganese(II) in this reaction.[15] In this study, we found that DMG slightly accelerates the reaction in the absence of metal ions, while in the presence of nickel (at a nickel:DMG molar ratios of 1:1 or above) the indicator reaction rate significantly increases (Figure 1). As it can be observed from the absorption spectra in the TMB–DMG–nickel(II)–$NaIO_4$ system, nickel exerts its negative catalytic action without activators (no DMG, *cf.* curves *1* and *2*). In the presence of DMG, an additional absorption peak at 450 nm appears (curve *3*), which corresponds to the orange TMB oxidation product. This maximum could not be attributed to the complex of nickel with DMG because it has a different absorption spectrum (curve *4*). Thus, the presence of DMG causes no change in the products of oxidation of TMB with periodate, but the first (green) product forms more rapidly and the second (orange) product of the deeper oxidation of TMB appears faster, which evidences the catalytic action of nickel.

The next question to be considered is in what form does nickel exhibit its accelerating effect. Under the conditions used (pH 6.8), nickel(II) bis(dimethylglyoximate) is supposed to form.[16] To study the catalytic action of nickel in the form of this complex, the latter was obtained by adding a 1% ammonia solution of DMG to a solution of nickel (100 mg dm^{-3}) and heating to 60–70 °C followed by filtration.[17] The resulting nickel bis(dimethylglyoximate) was treated with ethanol to yield a saturated ethanolic solution with a concentration[18] of 1.7×10^{-6} mol dm^{-3} at 25 °C. No difference in the catalytic activities of equal concentrations of nickel with an excess of free DMG and in the form of pre-synthesised nickel bis(dimethylglyoximate) was found. Probably, the same complex $Ni(DMG)_2$ is the catalytically active species in either case. It is known that DMG stabilises higher oxidation states of nickel (III or IV), which is widely used in analysis.[19] The catalytic action of nickel can be explained by $Ni^{II}(DMG)_2$ oxidation by periodate to form $Ni^{IV}(DMG)_2$, which oxidises TMB reducing to $Ni^{II}(DMG)_2$. The observed activating effect enables us to develop a procedure for the determination of nickel by the accelerating action of its complex with DMG in the oxidation of TMB with periodate.

Table 2 Determination of nickel(II) in well water using a TMB–DMG–$NaIO_4$ reaction and reference methods (n = 3, P = 0.95).

Method	Found nickel(II)/μg cm^{-3}
Proposed method	2.4±0.3
Voltammetry	3.2±0.9
AAS with ETA	3.3±1.2

Optimization of conditions for the determination of nickel. The pH dependence of the rate of indicator reaction with and without nickel was studied in a wide pH range with borate, phosphate and TRIS–HCl buffer solutions. Maximum differences in the rates of reactions with and without DMG were observed at pH 6.8 with a borate buffer. The effects of the concentrations of TMB and sodium periodate on the rates of TMB–Ni^{II}–$NaIO_4$ and TMB–DMG–Ni^{II}–$NaIO_4$ reactions were also studied. The formation of the blue-green product can be measured at periodate concentrations up to 4.3×10^{-4} mol dm^{-3}; at greater concentrations, this intermediate product rapidly transforms into the orange one. The following optimum concentrations were chosen: TMB, 1.3×10^{-4} mol dm^{-3}, $NaIO_4$, 2.2×10^{-4} mol dm^{-3}. For the TMB–DMG–nickel(II)–$NaIO_4$ reaction, the dependence of the reaction rate on the concentration of DMG was studied. The data presented in Figure 2 show that the rates of the indicator reaction both with and without nickel increase with the concentration of DMG, and at a certain concentration, reach a plateau. The optimum concentration of DMG is 8.5×10^{-4} mol dm^{-3}.

Under the above conditions, correlations of the reaction rate with the concentration of nickel were obtained in the range 0.5–3.0 μg cm^{-3} without DMG and in the range 3×10^{-4}–3×10^{-3} μg cm^{-3} in the presence of DMG. The metrological characteristics of the procedures developed for the determination of nickel are presented in Table 1. The negative catalytic effect does not provide the sensitivity as high as the positive catalytic effect. The procedure using nickel positive catalytic effect with an activator (DMG) exceeds in its sensitivity most of the known procedures for the determination of nickel by catalytic methods.[2–7,12,13]

For the developed procedures, we studied the interferences of various ions that exert appreciable effects on the indicator reaction.[15] Equal amounts of Fe^{III} and Co^{II}, as well as 0.1 μg cm^{-3} of Zn^{II}, Cd^{II} and Cu^{II}, interfere with the determination of 1 μg cm^{-3} of nickel using the procedure without DMG. In the presence of DMG, higher selectivity is observed: a 10-fold amount of Cd^{II} and a 100-fold amount of Zn^{II} interfere with the determination of 1×10^{-3} μg cm^{-3} of nickel, thus improving the selectivity by two and three orders of magnitude, respectively. Manganese(II) ions, which demonstrate an acceleration effect in the indicator reaction even at a concentration as low as 1×10^{-6} μg cm^{-3}, violently interfere with the determination of nickel by both procedures (with and without DMG). However, in the presence of DMG, an increase in selectivity by an order of magnitude was also observed.

Analysis of natural water. The test well water contained 0.004 μg cm^{-3} of manganese and 0.06 μg cm^{-3} of total iron; however, those were supposed to be present in the form of (pseudo)colloidal unreactive $MnO(OH)_2$ and $Fe(OH)_3$. For analysis, an aliquot portion (0.5 ml) was introduced into a test tube instead of a nickel solution (see the procedure above). The analysis was performed using the standard addition method. The results agree with those obtained by adsorptive stripping voltammetry[20] and AAS with electrothermal atomization (Table 2). The lower value obtained by the proposed kinetic method though being statistically insignificant may reflect the incompleteness of nickel extraction from humate complexes by DMG.

We are grateful to Dr. N. M. Sorokina and Dr. L. N. Bannykh for AAS measurements and to Dr. G. V. Prokhorova for her assistance in voltammetric measurements.

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Received: 18th November 2003; Com. 03/2189

Influence of Cu^{2+} ions on monolayer stability in an aqueous subphase and vesicle self-organization on the basis of the phosphorylated methanofullerene–lecithin system

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DOI: 10.1070/MC2004v014n05ABEH001896

The influence of Cu^{2+} ions on the state of mixed phosphorylated methanofullerene–lecithin monolayers and vesicles has been estimated.

Methanofullerenes are applicable to the production of new materials and in the synthesis of biologically active compounds.[1–4] Possible applications depend on the capability to form self-organised assemblies, stable Langmuir monolayers and three-dimensional networks.

Although the spreading of fullerenes on a water subphase in a Langmuir trough was reported,[5–8] the structure and stability of the films remained not optimal.

In the development of biosensors, it is very important to combine fullerene C_{60} derivatives with well-known self-organising amphiphilic compounds such as lecithins. Lecithins form stable monolayers and lipid vesicles composed of membrane-like lipid layers surrounding aqueous compartments. Therefore, the addition of lecithin to the methanofullerene system is an effective method for constructing mixed monolayers and vesicles.

We used methoxycarbonyl (dimethoxyphosphoryl) methanofullerene and its mixtures with lecithin to study the stability of monolayers and self-organization in the presence of Cu^{2+} ions.

The synthesis and structure of phosphorylated methanofullerene (P-methano-C_{60}) were described elsewhere:[9] analytical grade 1-palmitoyl-2-oleylglycero-sn-phosphatidylcholine (Sigma) was used. Surface pressure–area isotherms were measured in a rectangular trough made of polytetrafluoroethylene (200×137×3 mm). Measurements of pressure–area (Π–A) isotherms were made using a computer-controlled film balance system. The concentration of P-methano-C_{60} was 1×10^{-4} mol dm^{-3} in chloroform and the spreading amount of P-methano-C_{60} solution was 30 µl. Lecithin was dissolved in chloroform–ethanol. After solvent evaporation, a monolayer was compressed at a speed of 14 mm min^{-1}. The average velocity of compression is 1.2 Å^2 min^{-1} molecule^{-1}. In the compression-decompression processes, hystheresis was not observed.

The molecular structures of P-methano-C_{60} and lecithin are shown in Figure 1.

The isotherms showed an initial increase in the surface pressure in the region 2–5 mN m^{-1} for the liquid phase (Figure 2, curve *2*). The lines drawn to $\Pi = 0$ indicate the collapse area of the condensed monolayer and correspond to surface molecular area per molecule for close packed monolayers.

The limiting area per molecule, extrapolated to $\Pi = 0$, is 1.04±0.04 nm^2 (Figure 2). Assuming a close-packed hexagonal lattice, this value corresponds to an inter-headgroup spacing of 10.75 Å.

Lecithin, which exists in a zwitterionic form and produces a condensed film in the monolayer under water subphase, is a gel phase including associated water and producing the limiting mean molecular area 0.54±0.2 nm^2 (Figure 2, curve *1*). The Π–A isotherms of the mixed monolayers of P-methano-C_{60}–

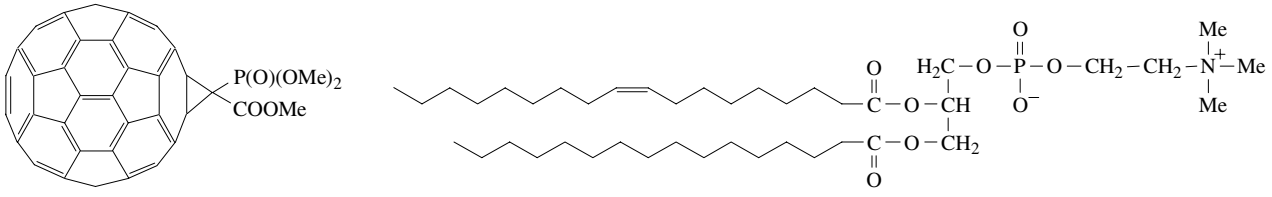

Figure 1 Chemical structure of methoxycarbonyl(dimethoxyphosphoryl)methanofullerene and 1-palmitoyl-2-oleylglycero-sn-phosphatidylcholine.