Rapid Quenchfluorimetric Determination of Nickel(II) in Some Real and Environmental Samples

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Abstract: A fluorimetric method for rapid determination of Ni at trace and ultratrace levels [1 ng/ml–1 μg/ml] has been developed. It is based on the efficient quenching action of Ni(II) on the native fluorescence ($\lambda_{em(max)} = 288$ nm, $\lambda_{ex(max)} = 444.8$ nm) of 4,7-diphenyl 1,10-phenanthroline disulfonate (bathophenanthroline disulfonate) solution at low acidities. The method is very simple, rapid and accurate with high precision (R.S.D. = 0.66% at 50 ng/ml). The method has been applied directly to mineralised solutions of several real and environmental samples and the results of nickel determinations are in excellent agreement with the certified values. It is a quick single-step method that requires no clean-up.

Key words: nickel(II), bathophenanthroline disulfonate, quenchfluorimetry, environmental samples.

Nickel traces are industrially important, environmentally pollutant, occupationally hazardous and biologically toxic and micronutrient [1]. Nickel toxicity causes different diseases, including asthma and cancer of the nose, lung and intestine [2]. Therefore, its trace and ultratrace analysis is of acute importance. AAS [3–6], GF-AAS [7–9] and even ICP-AES [10, 11] methods require pre-separation steps (e.g. solvent extraction using suitable chelating agents or ion-exchanger) for removal of matrix interferences vis-a-vis enrichment of the analyte concentration and for increasing the sensitivities, making the methods lengthy and expensive. Chemiluminescent methods with the noltrifluoracetone [12, 13] and luminol [14], based on the catalytic action of nickel(II), are subject to interference from various metal ions capable of activating (or inhibiting) the chemiluminescence reactions. Relatively high interferences and low sensitivity and precision are common disadvantages of chemiluminescent methods. Existing fluorimetric [15–23] methods are unselective and insensitive. There are other serious disadvantages as well. For example, the 1,10-phenanthroline method [17] and tetrakis(p-sulfophenyl) porphyrin method [22] are solvent extractive; in the latter case reaction occurs in a boiling water bath. Many coloured ions and heavy metal ions interfere in all cases. The fluorimetric method being presented here is simpler, more selective and more sensitive than these methods.

Experimental

Apparatus

All fluorimetric measurements were performed on a Shimadzu spectrophotofluorometer (RF-5000), equipped with a 150-W xenon lamp, colour video display, parallel-line thermosensitive printer recorder, 1 x 1 cm quartz cells, and a Shimadzu ASC-5 auto sample changer. Operational performance and sensitivity of the instrument were checked by running the Raman spectrum of distilled deionised water and the wavelength error was kept below ± 2.0 nm. Throughout the experiment both the excitation and emission bandwidths were fixed at 3 nm. An Electronics Corporation of India digital pH meter (model pH 5651) was used for measurement of pH; a Hanovia fluorescence UV lamp (model 11A) was used for preliminary qualitative fluorescence studies.

Reagents

All Chemicals used were of analytical reagent or equivalent grade and doubly distilled deionised water was used throughout. A standard Ni(II) solution (1 mg/ml) was prepared by dissolving 0.4784 g of nickel sulfate heptahydrate (Sarabhai M. Chemicals, A.R.) in 100 ml of water. This was standardised by EDTA titration [24]. The stock

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solution was diluted with water as required prior to use. A 0.1% (w/v) [1.693 × 10^{-3} M] sodium bathophenanthrolinedisulfonate [4,7-diphenyl-1,10-phenanthrolinedisulfonate] (Loba-Chemie Wien Fischamend) solution was prepared in water. This solution was stable for more than a month if preserved in a refrigerator. Other solutions prepared were: 1% (w/v) Na_2-EDTA (E. Merck, p.a.) and 0.2 N H_2SO_4 (95–98%, E. Merck).

Procedure

Into a 10-ml volumetric flask were added a volume of sample solution containing 0.01–0.1 µg or 0.1–1.0 µg or 1.0–10.0 µg of Ni(II) and, respectively, 0.3 ml of 10^{-4} M or 1.0 ml of 10^{-4} M or 1.0 ml of 10^{-3} M bathophenanthrolinedisulfonate solution. The solution was allowed to stand for 5 min, then 2–5 ml of 0.2 N H_2SO_4 was added. In the case of multicomponent systems, (e.g. real and environmental samples), 1ml of 1% (w/v) Na_2-EDTA was added as masking agent. The solution was diluted to volume with deionised water and the fluorescence intensity was then measured at 444.8 nm (excitation at 288 nm). The concentration of Ni(II) in the unknown sample was determined with the help of a concurrently prepared calibration graph.

Procedure and Sample Mineralisation for Real and Environmental Samples

Alloys. Solutions of alloys were prepared by dissolving 0.1 g of alloy in 2 ml of a mixture (1:1) of conc. HNO_3 and HCl with careful heating. The solution was cooled and diluted to 100 ml with water in a volumetric flask.

Environmental water. 50 ml of filtered environmental water samples were digested with 3 ml of conc. (2:1) HNO_3–H_2SO_4 mixture until white SO_3 fumes were evolved. It was diluted with 10–20 ml of water, filtered if necessary and the residue washed with water. The filtrate and washings were collected in a 50-ml volumetric flask and made up to the mark with water.

From suitable aliquots of the mineralised stock solutions, Ni(II) was fluorimetrically determined according to the procedure outlined, using Na_2-EDTA as masking agent.

Results and Discussion

Spectral Characteristics

The uncorrected excitation and emission spectra of 4,7-diphenyl-1,10-phenanthrolinedisulfonate solution containing 2 ml of 0.2 N H_2SO_4 per 10 ml total volume were measured. The wavelength maxima of excitation and emission were found to occur at 288 and 444.8 nm, respectively (Fig. 1).

Effect of Time

The studies on the effect of time showed (Fig. 2) that the maximum of fluorescence quenching was obtained 5 min after mixing and remained constant for up to 24 h. Longer periods were not studied.

Effect of Acidity

Changing the acidity showed that the maximum and constant fluorescence quenching was achieved with 2–5 ml of 0.2 N H_2SO_4 in the total 10 ml volume. This corresponds to 0.04–0.1 N acidity w.r.t. H_2SO_4 (Fig. 3).

Calibration Graph

The fluorescence intensity vs. Ni(II) concentration calibration graph is rectilinear within a total range of 1 ng/ml–1 µg/ml distributed over three ranges, 1.0–10.0 ng/ml, 10.0–100.0 ng/ml and 0.1–1.0 µg/ml Ni(II), for the convenience of fluorescence intensity measurements; typical calibration graphs are shown in Fig. 4. The precision of the method was studied. For 11 replicate determinations of 50 ng/ml of Ni(II), the stan-