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

Bijoli Kanti Pal*, K. Anand Singh, and Dipankar Chakraborty

Analytical Chemistry Division, Department of Chemistry, Jadavpur University, P.O. Box 17030, Calcutta 700032, India

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 [λ_ex(max) = 288 nm, λ_em(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, quenchofluorimetry, 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 thenoyltrifluoroacetone [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 spectrofluorophotometer (RF-5000), equipped with a 150-W xenon lamp, colour video display, parallel-line thermosensitive printer recorder, 1 × 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 band widths 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
solution was diluted with water as required prior to use. A 0.1% (w/v) 
\([1.693 \times 10^{-3} \text{ M}]\) 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) Na₂-EDTA (E. Merck, p.a.) and 
0.2 N H₂SO₄ (95–98%, E. Merck).

**Procedure**

Into a 10-ml volumetric flask were added a volume of sample 
solution containing 0.01–0.1 \(\mu\)g or 0.1–1.0 \(\mu\)g or 1.0–10.0 \(\mu\)g of Ni(II) 
and, respectively, 0.3 ml of \(10^{-4} \text{ M}\) or 1.0 ml of \(10^{-4} \text{ M}\) or 1.0 ml of 
\(10^{-3} \text{ M}\) bathophenanthrolinedisulfonate solution. The solution was 
allowed to stand for 5 min, then 2–5 ml of 0.2 N H₂SO₄ was added. 
In the case of multicomponent systems, (e.g. real and environmental 
samples), 1ml of 1% (w/v) Na₂-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. HNO₃ 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) HNO₃-H₂SO₄ mixture until 
white SO₃ 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 out-
lined, using Na₂-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 H₂SO₄ 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 H₂SO₄ in the total 10 ml volume. This 
corresponds to 0.04–0.1 N acidity w.r.t. H₂SO₄ (Fig. 3).

**Calibration Graph**

The fluorescence intensity vs. Ni(II) concentration cali-
bration graph is rectilinear within a total range of 
1 ng/ml–1 \(\mu\)g/ml distributed over three ranges, 1.0– 
10.0 ng/ml, 10.0–100.0 ng/ml and 0.1–1.0 \(\mu\)g/ml Ni(II), 
for the convenience of fluorescence intensity measure-
ments; 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-