



Quantitative Determination of Selenium and Development of Chemical Sensing Indicator Plates via New Synthesized Dye and its Application in Water and Plant Samples

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Abstract

A selective, simple, inexpensive and a new reagent for determination of selenium is proposed. This method is based on oxidation of hydroxylamine hydrochloride with selenite ions to nitrous acid, which in turn diazotizes sulfanilic acid which subsequently couples with NEDA to form magenta colored azo dye. The dye thus formed shows a maximum absorbance at 550 nm. The method obeys Beer's law in the range of 0.05 to 0.26 ppm of Se. Its molar absorptivity, Sandell's sensitivity, standard deviation and relative standard deviation were found 9.04×10^3 , 8.73×10^{-3} , 0.002, and 0.87% respectively. All the reaction parameters have been optimized. Interferences between the azo reaction and non targeted ions often present in environmental samples were investigated. The method has been successfully applied to the analysis of waste water and plant material. Chemical sensing strips were also been prepared and were successfully applied for detection of selenium in air and semi quantitative determination in water. The advantages of method are its high sensitivity, reproducibility, and the fact that measurement is simple, rapid and low cost.

Keywords: Diazotization, coupling, azodye, selenium, chemical sensing device, NEDA.

Introduction

Heavy metals are priority toxic pollutants that severely limit the beneficial use of water for domestic and industrial application¹. There are over fifty elements that can be classified as heavy metals, but only seventeen that are considered to be both very toxic and relatively accessible. Mercury, lead, arsenic, cadmium, selenium, copper, zinc, nickel, and chromium should be given particular attention in terms of water pollution². Heavy metals are present in the soil, natural water and air, in various forms and may contaminant food and drinking water³. Selenium is a naturally occurring element considered a link between metals and nonmetals because of its unique properties. It is found in nature in small concentration in rocks, plants, coal and fossil fuels. Volcanic eruptions, insecticides, fertilizers, smelting ceramics, metallurgical operations, glass rubber accelerators and electronic goods are major environmental sources of Se⁴. Selenium enters into natural water through seepage from seleniferous soil and industrial waste⁵. The automobile spare part market represents a potential source of selenium⁶. Certain industrial and agricultural- processes releases selenium as a byproduct. The maximum tolerance limit value (TLV) for human being is 0.1 mg/m^3 in air and 4ppm for water⁷. Currently, low concentration of aqueous Se concentration or speciation is analyzed either by ICP-MS, Hydride generation graphite furnace AAS or Ion chromatography hydride generation AES⁸⁻⁹. However, these techniques, although they provide high sensitivity are rather challenging and rely on complex

instruments and thus are expensive for regular analysis, particularly true for developing countries, where selenium toxicity is a well known problem.

Several methods for determination of selenium through complexation¹⁰⁻¹³, oxidative coupling¹⁴⁻¹⁵ and diazotized coupling¹⁶ have been reported.

This paper describes the detailed reaction scheme mechanism of a reliable and sensitive method based on a three step reaction (oxidation, diazotization and coupling) which produces a magenta colored azo dye that can be analyzed spectro- photo metrically at 550nm along with description of development of chemical sensing strips for detection of selenium in air and semi quantitative determination of water.

Material and Methods

Apparatus: All spectral measurements have been carried on digital spectro- photometer: - Systronic-166, BSM-13 and UV-visible spectrophotometer 2201.

Reagents: All reagents used were analytical grade chemicals. Double distilled water is used throughout the experiment.

Selenium solution: $80 \mu\text{g mL}^{-1}$ stock solution of Se was prepared by dissolving 219.015 mg of Na_2SeO_3 containing 80 μg of selenium in 100 ml of distilled water. $1 \mu\text{g mL}^{-1}$ working standard was prepared by appropriate dilution of stock daily.

Hydroxylamine Hydrochloride (HA): 10% aqueous $\text{NH}_2\text{OH}\cdot\text{HCl}$ was prepared by dissolving 10g of HA in 100ml of distilled water.

Sulfanilic acid (SA): 1% Sulfanilic acid was prepared by dissolving 1g SA in hot water.

Hydrochloric Acid: 1ml of 85% pure concentrated HCl was used for diazotization, 4M HCl was used for making up the final volume.

N-(1-naphthyl) Ethylene diamine dihydrochloride (NEDA): 1% NEDA was prepared by dissolving 1g NEDA in 2ml HCl and then made up to 100ml by distilled water.

Procedure: 1-4ml of sample is taken in 30ml graduated tube, 2ml of 10% hydroxylamine hydrochloride, 1ml of conc. HCl and 3ml of 1% sulfanilic acid were added to it. The solutions are shaken and heated at 50-60°C for 10-15 min kept for few seconds, then, 4ml of 1% NEDA are added and diluted to 15ml by 4M HCl and the absorbance is measured at 550nm. The reagent blank prepared in the same fashion shows negligible absorbance at 550nm.

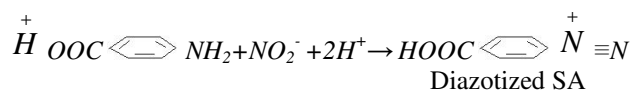
Results and Discussion

Reaction mechanism: The color reaction for the proposed system may be as follows:

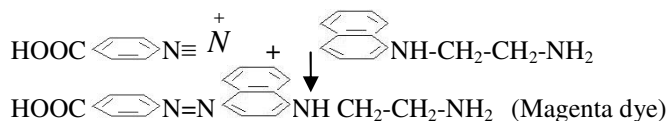
I Step: Selenite ions (Se IV) oxidizes $\text{NH}_2\text{OH}\cdot\text{HCl}$ to HNO_2



II Step: HNO_2 produced diazotizes sulfanilic acid producing a diazonium salt



III Step: Coupling takes between NEDA and diazotized SA, thus forming a stable magenta dye. The method is based on the oxidizing property of selenite ions in acid media.



Spectral Characteristics: The magenta colored dye formed exhibit maximum absorbance at 550nm. Reagent blank shows negligible absorbance in this range as shown by figure- 1.

Reaction conditions: Molarity: 4M HCl was found optimum for diazotization and color development, no color develops below 3M of HCl and reading increases above 4M of HCl if used. For making up the final volume 0.5 to 1.5M HCl was used.

Temperature: The reaction was studied for 0°C-100°C. Absorbance decreases below and above 50°C-60°C. On boiling

absorbance increases but blank reading too. Thus 50°C- 60°C was found optimum for color development. The dye was found stable for more than 20 hr.

Time: Absorbance was measured instantly, after 5 minutes heating, 10 minutes heating, 15 minutes, 20 minutes, 25 minutes and continuous increase in absorbance was observed till 10min, remains nearly constant till 15 minutes and then it start decreasing. Thus 10-15 minutes time was found optimum.

Reagent concentrations: Following concentrations of reagents were found optimum when reaction was studied for 1-5ml of each reagent:

Sulfanilic acid: 3ml of 1% Sulfanilic acid.

Hydroxylamine hydrochloride: 2ml Hydroxylamine hydrochloride

NEDA: 4ml of 1% NEDA

HCl: 1ml of 4M HCl for diazotization and 3-5ml of 1.5M final volume make up.

Effect of Co-pollutants: The method has been checked for its validity in presence of various co-pollutants and other foreign species. Interference of nitrite is masked by addition of sulphamic acid/sodium arsenite prior to analysis. The method was found to be free from most of the co-pollutants. The results obtained were given in table-1.

Table-1
Tolerance limit to various interfering ionic species

S. No.	Interfering ions (co-pollutant species)	Tolerance limit ($\mu\text{g mL}^{-1}$)
1	K^+, Cr^+	6×10^5
2	$\text{Mn}^{++}, \text{Ca}^{++}, \text{Mg}^{++}, \text{Na}^+, \text{Cl}^-, \text{CO}_3^{--}$	1×10^5
3	Al^{+++}	1.5×10^5
4	NH_3	2.5×10^5
5	Zn^{++}	2×10^5
6	$\text{Fe}^{+++}, \text{NH}_4^+, \text{SO}_4^{--}$	5×10^5
7	Cu^{++}	6×10^6
8	Hydrazine	1×10^3

Application: The method found its applicability in various real samples as described, data are given in table -2.

Selenium in polluted water: - To an aliquot (150-250ml) of sample contained in distillation flask, 1g of KI and 10ml of H_2SO_4 treated with 0.5 ml of saturated bromine water were added and the solution distilled under vacuum till copious fumes of SO_3 vapor were evolved. By this process all other forms of selenium are converted into selenium (IV). The distillate was collected in 10 ml of 5% hydroxylamine chloride solution and made up to a fixed vol. (50ml) and analyzed by the described procedure.

Selenium in plant material: 5g cabbage (spikes) was taken. 10 ml of conc. nitric acid was added and gently heated for 20 min. Then 0.5 ml of per chloric acid was added and contents were gently heated for 10 min. until the evaluation of ample fumes per chloric acid. 10 ml of water was added to the cooled residue and heated again for 10 min. then 5 ml of conc. HCl was added and heating continued for 10 min. the contents were diluted to 50 ml after adding 10 ml. of EDTA solution. An aliquot (1 ml) of sample was taken and selenium was determined as recommended.

seconds. The paper turned magenta indicating the presence of selenium. As little as 0.2 µg of selenium can be detected by using test paper strips.

Detection and semi quantitative determination in water: The test papers had also been successfully used for water to detect as low as 0.02µg selenium. Semi quantitative determination had been done by comparing the color with standard samples prepared.

Indicator Tubes: Detection and semi quantitative determination of Se in water has been done using above method. Simple glass plates of size (2 x 6 cm) having uniform thickness were taken and a slurry of silica was pasted of about 1mm thickness. After drying the plate in oven at 100⁰C for an hour it was impregnated with HA and Conc. HCl, dried in a temperature controlled oven at 50⁰C-60⁰C, then impregnated with SA, again dried at 50⁰C-60⁰C, finally impregnated with NEDA and again dried at the same temperature. These indicator plates were found to be stable for about 10 days if kept in a well stoppered bottle. A single drop of water containing Se will indicate its presence on these plates in form of magenta color appearance. As little as 0.02 µg of selenium can be detected using these plates.

Table- 2

Presence and Recovery of selenium in various real samples

S. No.	Sample (amt. g)	Se added (µg)	Total Se (µg)	%
1	Cabbage(5g)	10	9.43	94.3
2		20	18.85	94.2
3		30	28.75	95.8
4	Waste water(250ml)	10	9.8	98
5		20	19.7	98.5
6		30	29.5	98.3

Preparation of Test Paper: The method has been used to prepare test papers for detection and semi quantitative determination of selenium in air and water. Whatman no. 41 filter paper stripes (1x5 cm) were cut, dipped in HA and Conc. HCl, dried in a temperature controlled oven at 50⁰C- 60⁰C, then dipped in SA, again dried at 50⁰C-60⁰C, finally dipped in NEDA and again dried at the same temperature. These test papers were found to be stable for about three weeks, if kept in a well stoppered bottle.

Detection in air: At the time of testing selenium in air, the test papers were exposed to vapors of selenium sample for a few

Conclusion

The proposed method is cheap, rapid and environment friendly, highly sensitive and easily employable as compared with the method based on same principle as reported in table-3.

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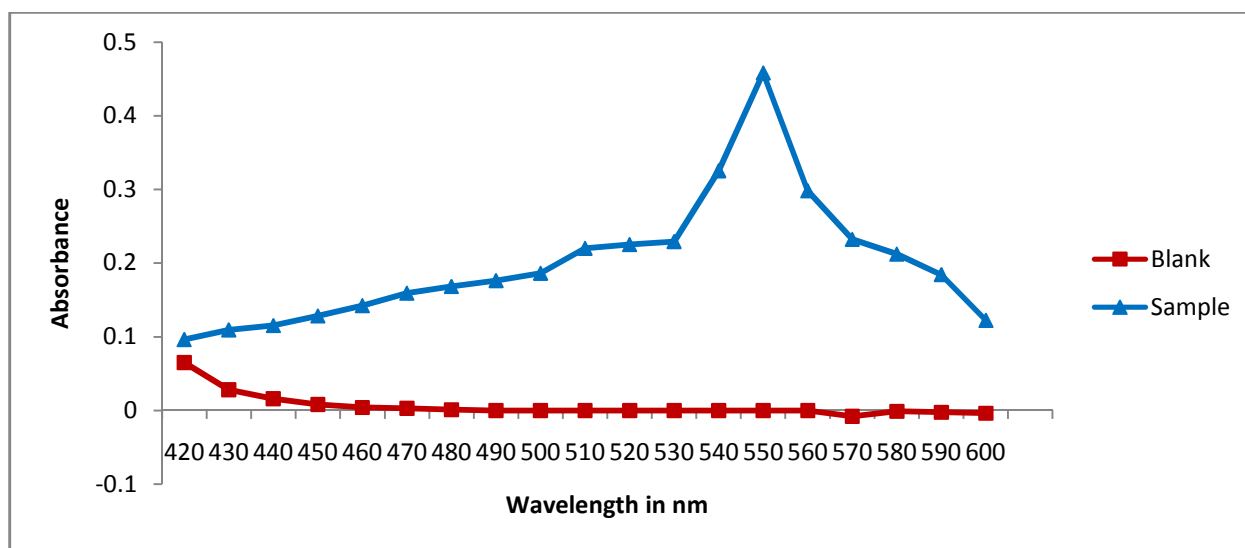


Figure-1
 Absorbance Spectra of Sample with respect to Blank

Table-3
Comparison with other reported methods

S. No.	Reagents used	Medium/pH	λ_{max} .	Beer's Law range(ppm)	Special remarks
1	3,3'Diaminobenzidine ¹⁷	Aqueous/2-3	420	0.1-10	Colored salts interfere
2	J-acid ¹⁰	Acidic/ 1-2.5	520	.03-0.3	Less sensitive
4	HA, PNA, NEDA ¹⁶	Acidic/ 2	545	0.1-2.5	Sensitive but more amount of chemicals is used, time consuming, High blank
5	HA, SA,NEDA (Proposed method)	Acidic /2	550	0.05-0.26	Highly sensitive, cheap, rapid, negligible blank

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