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Aescin as Novel Green Analytical Reagent for Optimization, Validation and Application of Spectrophotometric Method for Determination of Nitrite in Drinking and Environmental Water Samples

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Abstract

Replacement of toxic reagents was established to attain the standards of clean chemistry. Novel green reagent for simple and highly sensitive spectrophotometric determination of trace amounts of nitrite in environmental samples was developed. The method is based on the oxidation of 3-methyl-2-benzothiazoline-hydrazono hydrochloride hydrate (MBTH) in hydrochloric acid medium by nitrite and coupling with Aescin to yield blue colored .The blue color, which has an absorbance maximum at 680nm are stable for 3h. The method obeys beer's law in concentration range 0.15-1.20µgml^{-1}andmolar absorptivity 2.71x10^{4}l mol^{-1}cm^{-1}. The optimum reaction conditions and other important analytical parameters were determined. Interference by various cations and anions has been investigated. The proposed method has been applied to the analysis of nitrite content of tap water, well water and soil samples. The method was evaluated in terms of Variance ratio F-test and Student's t-test to found out the significance of proposed method over the reference method.

Keywords: Aescin; Green reagent; Environmental samples; Spectrophotometric

Introduction

The nitrite ion is an important intermediate step in the nitrogen cycle and is present in soils and surface waters because of its high solubility in water [1]. The increasing eutrophication of natural waters and the salification of aquifers may pose health problem caused by cyanosis in-vivo resulting in the formation of carcinogenic, mutagenic and teratogenic nitrosamines and nitrosamides [2].Besides, nitrite entering in bloodstream can oxidize the iron of hemoglobin producing metahemoglobinemia, which inactivates oxygen carrying capacity causing metahemoglobinemia. In adults, this process is reversible; however infants can die by asphyxia, a disease called "syndrome of the blue baby" [3]. Therefore, elucidation of nitrite concentration is desirable from the stand point of environmental analytical chemistry. The most important of principles of green chemistry [4], that are directly related to analytical chemistry 1-Prevention of waste generation 2- Design for energy efficiency 3-Safer chemistry to minimize the potential of chemical accidents 4-Safer solvents and auxiliaries.

J. Namies´nik has proposed the term green analytical chemistry [5,6] where search for less toxic compounds and processes with reduced waste generation should be an aim in the development of new methods.

Nowadays, green analytical methodologies are well established for environmental monitoring. However, the majority of methods generate chemical wastes, which contribute to environmental pollution [7].

In some situations, the chemicals employed are more toxic than the species being monitored. As a consequence, some environmental analytical chemists are focusing this work on the development of methodologies less harmful to human and to the environment. Nowadays, in the development of a new analytical method or a procedure the amount and toxicity of the reagents used and the wastes produced are as important as any other analytical feature. For example, the analytical method based on reaction N-(1-napthyl) Ethylenediamine hydrochloride (NEDA) with sulfanilamide to yielding an Azo dye is procedure for environmental monitoring of nitrite. However, this method uses reagent(s) or generates chemical wastes, which are moretoxic than the species being monitored [8].

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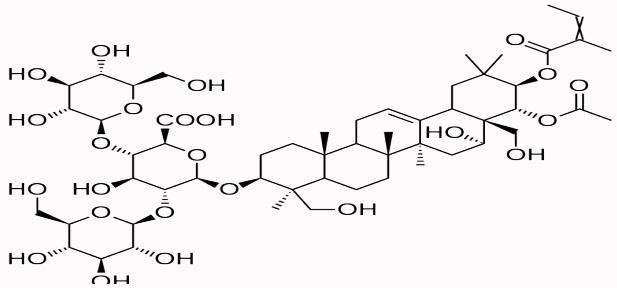

Figure 1: Structure of Aescin.

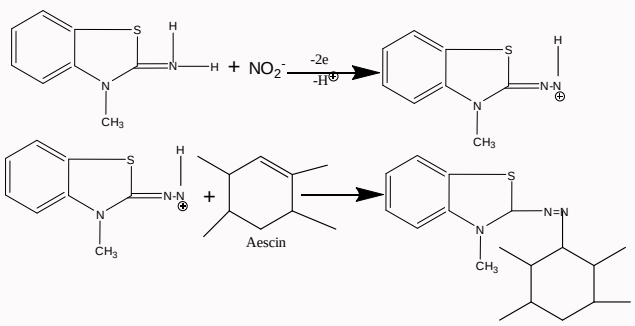

Figure 2: The proposed reaction mechanism between MBTH and Aescin.

As a consequence, the analytical methods not meet basic principles of Green Chemistry [9] which not acceptable. Hence, there is a great need to develop methods which are less harmful to human and to the environment.

An extensive literature survey revealed that many analytical methods have been reported for the analysis of nitrite in environmental samples include: high performance liquid chromatography (HPLC) [10–13], electrochemistry [14–16], optical analytical techniques [17–19] and visible spectrophotometric methods which are convenient, sensitive and are relatively inexpensive. These methods employ different routes for determination of nitrite ion [19–31]. Most of the spectrophotometric methods based on diazo-coupling with high sensitivity, but often have drawbacks of diazotization, pH, temperature and coupling time dependence. Besides, these methods often use large sample volumes of toxic or carcinogenic reagent(s), which makes it outside green chemistry [32].

With the objective of utilizing the non-toxic chemicals like natural product we introduce Aescin (cosmetic producte) (Figure 1). As novel green analytical reagent for determination nitrite spectrophotometry as chromogen and MBTH as electrophilic coupling reagent. Based on this, highly sensitive, selective and rapid method was developed and applied for the determination of nitrite in drinking and environmental water samples. Besides, the reagents meet main goal of the green analytical chemistry is to take into consideration the amount and the toxicity of reagents consumed, and, consequently, the volume and the toxicity of wastes generated during method development.

Experimental

Reagents

The reagents were used without further purification. Aescin (Sami Labs, India) and MBTH were from Aldrich. Sodium nitrite solution of 2.176 x 10^{-2} M (1000µg nitrite/ml) in 1000mL volumetric flask was prepared by dissolving 1.500g sodium nitrite (pre-dried at 110C° for 4h) in water. Required standard solution of (2µg nitrite/ml) was prepared by diluting with water 2ml of standard sodium nitrite solution to 1000ml. Stock solution (0.25% w/v) of Aescin was prepared by dissolving 250mg in 2% sodium lauryl sulphate in a 100-ml volumetric flask and made up to the mark. Solution (0.05% w/v) was prepared by dissolving 0.05g of MBTH and diluting quantitatively to 100mL with distilled water.

Table 1: Spectral data for the determination of nitrite using Aescin as chromogen reagent.

parameter	
Color	Blue
λ_{max} (nm)	690
Stability (h)	3
Beer's law (µg ml^{-1})	0.15 -1.20
Recommended ion concentration (µg ml^{-1})	0.50
Molar absorptivity (L mol-1cm^{-1})	2.71 x 10^4
Sandell's sensitivity (µg cm^{-2})	0.0017
Detection limit (µg mL^{-1})	0.053
Regression equation*:	
Slope (a)	0.489
Intercept (b)	-0.1473
Correlation coefficient	0.9813
Reaction time (min)	5
% R.S.D**	0.532

*y= ax + b where x is the concentration of nitrite in µg mL-1; **Relative Standard Deviation.

Apparatus

All spectral and absorbance measurements were carried out on UV-VIS spectrophotometer UVIDEC-610 type with 1.0-cm matched cell (JASCO, TOKYO, JAPAN) was employed for measuring the absorbance.

General procedure

1ml of Aescin (0.25% w/v), 1ml of 2M HCl and 1ml of MBTH (0.05% w/v) were added to a series of 25ml calibrated flasks appropriate nitrite aliquots containing know concentration, and the mixture shaken thoroughly and allowed to stand for 5min and the volume was make up with ethanol. Absorbance at 680 nm was measured in 1.0cm quartz cell against reagent blank which was prepared without nitrite. The optical characteristics are detailed in the Table 1.

Results and Discussion

The mine objective of this paper was to avoid diazotization reactions and to make the method greener. Consequently, the quantitative property of nitrite have been exploited to oxidize and subsequently couple with Aescin to yield blue color which forms the basis for spectrophotometric determination [33,34] as shown in Figure 2. These experiments confirmed that the proposed reaction was oxidative electrophilic coupling reaction. Not belong to diazotization reaction; instead, they followed an alternate route to produce color based on Key parameters that influence the performance of the proposed method were studied in order to establish the optimum working configurations. All the data given and % R.S.D. in the optimization steps for both physical and chemical parameters are the mean values from successive determinations. All the optimization steps were carried out with a chosen nitrite concentration as we mentioned in Table 1.

Table 2: Determination of the nitrite in different environmental samples.

Sample	Nitrite added µg ml^{-1}	Proposed method		Reported method			
		Nitrite recovered µg ml^{-1}	Recovery % ± RSD*	Nitrite recovered µg mL^{-1}	Recovery % ± RSD*	*t*-value**	*F*-value***
Tap water	0.5	0.506	101.20 ± 0.48	0.501	100.20 ± 0.2	2.2	5.21
	0.7	0.699	98.80 ± 0.81	0.703	100.40 ± 0.83	1.86	4.13
Mineral water	0.5	0.492	98.40 ± 0.30	0.496	99.20 ± 0.46	1.1	1.45
	0.7	0.689	98.40 ± 0.50	0.692	98.80 ± 0.55	0.98	2.37
Well water	0.5	0.489	97.80 ± 0.80	0.495	99.00 ± 0.49	1.8	1.95
	0.7	0.709	101.30 ± 0.60	0.688	98.30 ± 0.78	1.5	6.03
Soil samples	0.5	0.489	97.80 ± 0.80	0.495	99.00 ± 0.49	1.67	3.25
	0.7	0.692	98.80 ± 0.55	0.703	100.40 ± 0.83	2.1	1.68
Manured garden soil	0.5	0.495	99.00 ± 0.49	0.496	99.20 ± 0.46	2.5	2.43
	0.7	0.703	100.40 ± 0.83	0.692	98.80 ± 0.55	2.04	3.2
Farmland soil	0.5	0.496	99.20 ± 0.46	0.492	98.40 ± 0.30	2.2	1.53
	0.7	0.489	97.80 ± 0.80	0.689	98.40 ± 0.50	1.91	3.2
Roadside soil	0.5	0.485	97.00 ± 0.37	0.501	100.20 ± 0.20	0.55	2.11
	0.7	0.791	98.90 ± 0.85	0.689	98.40 ± 0.50	0.83	2.84

*Average of 5 determinations ± relative standard deviation; ** Tabulated t-value at 95% confidence level is 2.78 ;*** Tabulated F-value at 95% confidence level is 6.39.

Parameters

The parameters in visible spectrophotometric procedure control the extend of the reaction and responsible for the optimization of the concentration of the reagents and the order of addition of the reagents. Since the proposed method relies on the measurement of the absorbance; anything that affects the absorbance will have pronounced effect on the performance of the methods.

Wavelength determination: In order to get results with minimum interferences, it is necessary to find out the optimum wavelength for nitrite determination in the proposed method. This wavelength must be specific for the quantitative and specific monitoring of the nitrite-MBTH-Aescin. The wavelength of maximum absorbance was identified by scanning the product of nitrite MBTH-Aescin over the range 300–800 nm with a specord 50 UV-vis spectrophotometer. A wavelength with range690 nm for method was found to be optimum for getting the best results Table 1.

Effect of reagents and acid concentration: The effect of Aescin reagents was studied in the range of 0.10 – 10.00 ml of a (0.25% w/v) solution to achieve the maximum color intensity. A volume of 0.50 – 3.00 ml of the solution was necessary. Hence, 1ml of (0.25% w/v) solution in water in 25-ml standard flask was selected for further studies, under optimized conditions. The maximum intensity of the blue color was achieved in hydrochloric acid medium.

Preliminary investigations showed that hydrochloric acid was better than sulphuric, phosphoric or acetic acid. Maximum intensity of the blue color was achieved in the range of 1-5ml of 2M HCl. Therefore, 1ml of 2M HCl in 25-ml was used for getting the best results. Similarly the same procedure was adopted to know the amount of MBTH required for getting constant and maximum color intensity. It was found that a volume of 0.50 – 3.00 ml of the solution is necessary. Hence, 1ml of (0.05% w/v) MBTH solution was selected to get reproducible results. Experiments were carried out to optimize temperature and time of the reaction. It was found that the maximum color developed within 3min at room temperature and remains almost stable for about 4h. Increase in the temperature decreases the intensity of the blue color. Hence, 3min reaction was at room temperature sufficient for the routine analysis.

Order of addition of reactants: During the course of the investigations it was observed that the sequence of addition of reactant was also important as it influenced to great extent the intensity and the stability of the colored product to a greater extant. The sequences:

(i) Aescin-acid-nitrite–MBTH and (ii) nitrite-acid-Aescin-MBTH gave less intense and unstable color. While, (iii) nitrite - Aescin -acid-MBTH gave more intense and stable blue color. This was expected as the sequence (i) and (ii) produced radical cation. While, in (iii) electrophilic reaction was evident.

It was found that the blue color formed in the reaction was not affected after 5min and remained constant upto 3h therefore 5min was selected as the reasonable time in the absorbance study.

Analytical figures of merit: The proposed spectrophotometric method was evaluated under the optimum conditions with respect to linearity, accuracy, precision and interference.

Linearity (bear's law application), accuracy, precision: The linearity of the spectrophotometric method for the determination of nitrite was evaluated under optimum conditions. The regression calibration equation obtained under optimum conditions for nitrite with Aescin was: Y= -01473 + 0.4890X; r = 0.9813 and n = 7, where Y is the absorbance and X is the nitrite concentration as µg ml^{-1}. The calibration curve was linear over the range 0.15–1.20 µg ml^{-1}. The detection limit gives an indication of the lowest concentration of nitrite that can be distinguished from the backgrounds absorbance with 99% certainty. The detection limit was calculated as follows (Dl = 3.3δ/m), [where "δ" the standard deviation of the blank, "m" is the slope of the calibration curve]. Keeping Aescin as an example the calculated detection limit was 0.053µg ml^{-1}of nitrite.

The accuracy of the proposed system was evaluated by comparing the results obtained with environmental samples (from well, tap water and soils) using the proposed spectrophotometric method as well as the standard spectrophotometric method [32]. The results from the proposed spectrophotometric method compared very well with those from the standard method. The % R.S.D. was found to be

<1.3 (n = 5). The proposed method was found as accurate and precise as that of official method.

To further establish the validity and accuracy of the proposed method, recovery tests by standard addition method were performed. Known amount of standard solutions at two different levels were added to a fixed amount of real sample and the mixtures were re-analyzed by the proposed procedure; each test was repeated five times. The results presented in Tables 2show good recoveries and non-interference from commonly were presented in the real sample.

Interferences: The effect of possible interference was studied at nitrite concentration of 0.5µg ml^{-1}using Aescin (0.25% w/v) and MBTH (0.05% w/v). To study the selectivity of the proposed method, the effect of various chemical species on the determination of nitrite was tested under the optimal conditions. The tolerance limit was defined as the concentration of added ion causing less than ± 3% relative error for the nitrite determination. The following ions which did not interfere even when their concentrations was 1000-fold excess over nitrite concentration were SO_4^{2-}, CO_2^{2-}, Mg^{2+}, CH_3COO^-, K^+, Na^+, Cl^-, F^-, Cd^{2+}, Ca^{2+}, and EDTA. The ions Cu^{2+}, chloramine-T and chloramine-B interfered at 1.0 µgml^{-1}. Ions such as, Fe^{3+}, $Cr_2O_7^{2-}$, Mn^{7+} interfered seriously.

Application to polluted waters and soil samples: Samples were collected in wide-mouthed plastic vessels at different points from the source. Samples of potable water were collected from different taps and different packaged water bottles. The samples were frozen at 0C° within 1 h of collection. Samples were filtered through a Wathman No. 41 paper before analysis.

Samples of manures garden soil, farmland soil and roadside soil were collected. Each sample was broken up into lumps, and a 5-g portion dried at 55C° in an over for12-16 h. The dried sample was ground, passed through a 2-mm mesh sieve and transferred to a Whatman No. 50 filter paper on a Buchner funnel. Sufficient water (containing 1 or 2 drops of concentrated sulphuric acid) was poured on to soak the soil completely. After a few minutes, gentle suction was applied and the soil was washed with doubly distilled water until about 250ml of filtrate was collected. The filtrate was made up to a standard volume and aliquots were analyzed, as shown in Table2.

Conclusion

First -ever color formation based on an oxidative coupling reaction of Aescins and MBTH are proposed. The proposed method is simple, selective and reproducible. The method requires low cost equipment and the reagents are safe for health. The method tolerates more to the foreign ion effects than most of the methods do. Furthermore, the use of Aescins as new spectrophotometric reagent in the determination of environmental toxic substance will open up new area of research.

The proposed method, besides being simple, inexpensive, sensitive and precise as compared to the existing methods also claim the advantage of determination without the need for extraction or heating. The method does not involve complicated reaction conditions. The proposed method has got significant advantages over other existing methods in terms of simplicity and was free from most of the interfering substances. Statistical analysis of the results revealed that the proposed method yield as accurate and reproducible values as that standard method in the determination of nitrite in various soil and water matrices. Applications of the method in the determination of nitrite in a variety of real natural samples have demonstrated its practical utility.

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