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Determination of trace residual chlorine in drinking water by spectrophotometric method at Churu district Rajasthan

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Abstract
The method is based on the reduction of chlorine by an electrophilic coupling reagent, 3-methyl-2-benzothiazoline hydrazono hydrochloride hydrate (MBTH) and subsequent coupling with NEDA. An improved method using N-1-Napthylethylenediamine dihydrochloride (NEDA) as a chromogenic reagent for determination of residual chlorine is proposed. The blue color formed in the reaction showed maximum absorbance at 610nm and obeyed Beer’s law over the range 0.3-4.2ppm. The molar absorptivity and Sandell’s sensitivity values were 3.14×10^{3} L mol^{-1}cm^{-1} and 0.102µg cm^{-2} respectively. The performances of proposed methods were evaluated in terms of student t-test and variance ratio F-test which indicated the significance of proposed methods over the reference spectrophotometric method. The proposed methods were successfully applied in determination of residual chlorine in drinking water and environmental water samples.

Keywords: chlorine, water, spectrophotometer, residual

Introduction
Public drinking water, waste water, and industries uses chlorination for routine water treatment process for disinfecting and improvising the quality of water. Both the reagents undergo hydrolysis in water to form hypochlorous acid (HOCl) and hypochlorite ion (ClO^-). Chlorine is added to water either as chlorine gas (Cl) or as hypochlorite solution (NaOCl). A mixture of HOCl and OCl is referred to as free available chlorine. While, the addition of chlorine to waste water containing ammonia and organic nitrogen compounds may result in the formation of toxic chloramines depending upon the relative amounts of reactants present, temperature and pH. These chloramines are broadly classified as inorganic and organic. While, the organic chloramines are produced by the reaction of chlorine with amino acids and proteins present in wastewater. Besides, Chloramines may also result in the formation of chloroform, bromoform, bromodichloromethane and chlorodibromomethane together these four are called trihalomethanes (THM) or combined chlorine. The inorganic chloramines are formed by the reaction of chlorine with free ammonia. A number of studies on animals have shown that THM are carcinogenic, mutagenic and/or teratogenic. However, there is no conclusive evidence to indicate that THM at the levels which they occur in potable water may pose any serious health threats to human. Despite a large number of alternative disinfectants available, still no disinfectant offers as many advantages as chlorine in terms of convenience, reliability, ease of use and measurement and cost effectiveness. Thus chlorination of water still provides obvious benefits to public health that greatly exceed the danger posed by THM. Because of the widespread use of chlorine as chemical disinfectant there is a continuing interest in the development of analytical methods that are simple, sensitive, selective and rapid for the determination of various forms of chlorine in environmental matrices. Free residual chlorine is that portion of chlorine injected into water remaining as molecular chlorine (HOCl and/or OCl), while combined residual chlorine is the chlorine injected into water, which combines with ammonia or nitrogenous compounds, commonly referred to as THM. Amongst the various forms of chlorine, total residual chlorine, which is the free residual chlorine plus the combined residual chlorine, is of paramount importance. Methods having different efficiency and convenience have been developed for the determination of chlorine in aqueous samples, which include electro analytical, chromatographic and optical methods. There is a continued effort in the development of analytical methods for the determination of total residual chlorine (henceforth referred to as residual chlorine) in drinking water and environmental water samples. The most widely accepted spectrophotometric methods are based on the oxidation reaction of aromatic amines such as o-tolidine and 4-nitrophenylhydrazine forming colored products. Among optical methods simple visible spectrophotometric methods take precedence over chemiluminescence and UV-methods because of complexity involved in the chemiluminescence procedures and lack of selectivity of UV-methods. On account of the fairly high reactivity of these reagents, specification of residual chlorine is either troublesome or necessitates very careful control of the reaction conditions besides, the use of o-tolidine is restricted on account of its carcinogenic properties.

These kits although expensive but are stable while normal reagents have a fairly short shellfire. Besides, bromine, iodine and bromo-amines interfere by giving the same colored product with DPD. N, N-diethyl-p-phenylenediamine (DPD) is evidently the most widely used spectrophotometric reagent for the determination of chlorine in water sample. Ready kits are available for this and extensively used. Oxidizing agents such as ozone, chlorine dioxide, permanganate, iodate, chlorate and MnO also interfere, if their concentration exceeds 0.03 mg L. The decrease of methyl orange by chlorination has been reported but the spectrophotometric method has a determination limit of about 2µg/ml. The Thio-Michler's ketone method is sensitive to chlorine but lacks selectivity as other chlorine species and mercury (II) can also give a positive response. The express test done by using indicator papers has a special significance in the semi-quantitative determination of residual chlorine. Unfortunately, the sensitivity of such tests, in many cases is not high enough.

In response to the increasing concern over chlorine determination, we report simple and sensitive spectrophotometric method based on the use of NEDA as chromogenic reagent in presence of 3methyl-2-benzothiazoline-hydrazono Hydrochloride hydrate(MBTH) as an electrophilic coupling reagent for the determination of residual chlorine, and their application in drinking water and environmental water samples.

Materials and Methods

Apparatus

UV-VIS spectrophotometer UVIDEC-610 TYPE with 1.0-cm matched cell (Jasco, Tokyo, Japan) was employed for measuring the absorbance.

Reagents

Chlorine stock solution was prepared by mixing about 10g of bleaching powder, 1g of potassium permanganate crystals in 50ml of distilled water, 5ml of concentrated hydrochloric acid was added, the chlorine gas released was collected in 250ml standard flask and made up to the mark with distilled water. The concentration of chlorine solution was standardized iodometrically using standard titration method. Solutions of the required strength were prepared by diluting this stock solution with distilled water. The solutions were stable for 1 week. NEDA and MBTH were procured from Aldrich, USA. Fresh solutions of NEDA (0.1% w/v) and MBTH (0.05% w/v) was prepared by dissolving in distilled water. MBTH solution was stored in amber bottle to protect from the sunlight. Solutions of diverse ions were prepared by dissolving their corresponding salts. All reagents were of analytical grade and were used as received. DPD colorimetric method was followed as described in the literature.

Procedure

Aliquots of standard solution of chlorine, 1.0ml of 0.05 % (w/v) MBTH and 1ml of 0.1 % (w/v) NEDA were taken in a series of 25-ml calibrated standard flasks and kept aside for 20min at room temperature. Blue color obtained was made up to the mark with distilled water. The absorbance was measured at 610nm against the corresponding reagent blank prepared under identical conditions but without chlorine and the calibration graph was constructed. Concentration of chlorine in test solution was calculated from the regression equation computed from the Beer's law data as a reference.

Results and Discussion

3-Methyl-2-benzothiazoline hydrazone hydrochloride hydrate (MBTH) was first introduced for the Determination of aromatic amines and iminoheteroatomic compounds and aliphatic aldehydes. Later, it was extended for the determination of a large number of organic compounds such as those containing methylene groups, as well as with carbonyl compounds, Schiff's bases, aromatic hydrocarbons, saccharides, steroids, olefins, phenols, and furfural and heterocyclic bases. MBTH has often been applied in clinical, biochemical, and pharmaceutical, insecticidal and in flow injection analysis. N-1Napthylethylenediamine dihydrochloride (NEDA) was earlier used to couple with hydroazino groups of 4-nitrophenylhydrozone to give azodye. However, the diazotization reaction has limitations of temperature, time of reaction and toxicity of the reagents. Hence, electrophilic coupling reactions were adapted to yield the derivatives.

Reaction mechanism

The chemical reaction in the present spectropho- tometric study of residual chlorine involves the reduction of the chlorine by MBTH. The oxidized MBTH subsequently couples with NEDA to form a blue product having at 610nm. The color intensity remains constant up to 24h. The factors affecting the color development, reproducibility, sensitivity and adherence to Beer's law were investigated by optimizing the analytical variables.

Spectral characteristics

The absorption spectrum of the blue colored com- plex with residual chlorine shows a wavelength of maximum absorption at 610nm. The reagent blank shows negligible absorption at this wavelength.

Optimization of analytical variables

The reagents concentrations and quantity needed as also the reaction conditions were optimized to arrive at a standard procedure. Each parameter was optimized by setting other parameter constant.

Order of addition

The sequence of addition of reactants is also important as it influenced to a great extent to the intensity and the stability of the color product. The sequence (i) substrate+NEDA+MBTH gave no color. While, the orders (ii) NEDA+MBTH +substrate (iii) substrate+MBTH+NEDA display intense. Between order (ii) and (iii) the order (iii) gave more intense hence it was selected for further work.

Effect of MBTH

It was found that 1.0ml of 0.05% (w/v) MBTH was enough to get a blue color with maximum absorbance at 610nm. There was very negligible change in the absorbance of the colored products for higher added concentrations of MBTH.

Effect of NEDA

The maximum color development was obtained when 0.5-3.0ml of 0.1% (w/v) solution of NEDA was used in the procedure. The change in the absorbance was negligible at higher added concentrations up to 5.0ml. Therefore 1.0ml of was found optimum for color development.

Effect of temperature

Increase in the temperature decreased the intensity of the blue color. Hence, development of the blue color was carried out at room temperature. It was observed that the colored products were stable up to 24h.

Table 1: Spectral data for the determination of residual chlorine using MBTH as electrophilic coupling reagent

S. No.	Parameters	
1	Color	Blue
2	λ max (nm)	610
3	Stability (h)	24
4	Beer's law(µg ml)$^{-1}$	0.3-4.2
5	Recommended ion concentration (µg ml)$^{-1}$	1.6
6	Molar absorptivity (L mol^{-1}cm^{-1})	3.14×10^{3}
7	Sandal's sensitivity (µg cm)$^{-2}$	0.102
8	Regression equation Slope(a)	0.147
9	Intercept(b)	0.0677
10	Correlation coefficient	0.9856
11	Reaction time(min)	20

*y=ax+b where x is the concentration of residual chlorine in µg ml^{-1}

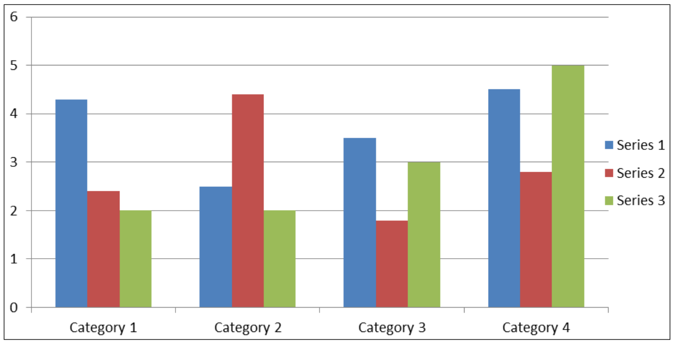

Fig 1

Table 2: Determination of residual chlorine in drinking water and environmental water samples

Sample	Chlorine Added(µg ml^{-1})	Chlorine recovered from the proposed method (µg ml^{-1})*	Chlorine found in the sample by DPD method	Student's t value (±)	F value(±)
Well water					
Well 1	0.50	0.68	0.66	2.0	2.6
Well 2	0.50	0.69	0.68	1.9	1.6
Well 3	0.50	0.66	0.68	1.8	1.9
Tap water					
Day 1	0.50	0.76	0.77	1.5	1.9
Day 2	0.50	0.78	0.80	1.0	2.0
Day 3	0.50	0.78	0.79	1.3	1.6
Lake water					
Day 1	0.50	0.62	0.63	1.9	2.3
Day 2	0.50	0.66	0.65	1.8	1.8
Day 3	0.50	0.64	0.65	1.0	1.9

* NEDA+MBTH method

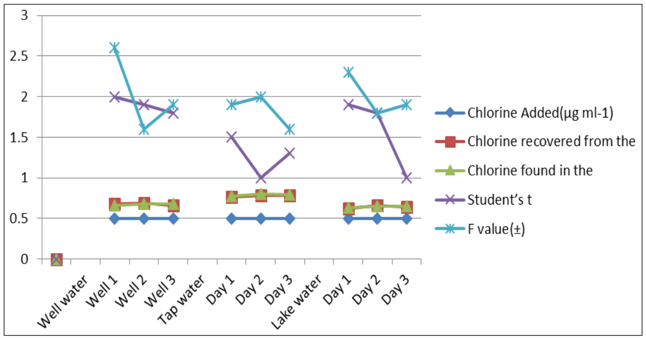

Fig 1

Analytical parameters

To determine the Beer's law limits, varying amounts of chlorine was reacted with a fixed volume and concentrations of MBTH and NEDA under the specified conditions and specific time. A linear correlation was found between absorbance values at in the range 0.3-4.2ppm. The apparent molar absorptivities, correlation coefficients, intercept and slopes, for the calibration data are presented in TABLE 1. The values in the table show negligible intercept as by the regression equation, Y=ax+b.

Effect of reaction time

Experiments were conducted to optimize the time needed in the determination of residual chlorine. It was found that the blue color formed in the reaction was not affected after 10min and remained constant up to 24h. Therefore 20min was reasonable for the absorbance study.

Interferences

Interference of foreign species were investigated by analyzing 2.4ppm standard solution of chlorine to which increasing amounts of interfering species salts of anions and cations were added. The tolerable limit of a foreign species was taken as a relative error not greater than 3%. It was found that 100ppm of cations like, barium acetate, barium nitrate, magnesium sulphate, zinc sulphate, anions like potassium iodide, sodium fluoride, sodium nitrate, sodium sulfite and 10ppm of lead nitrate, did not interfere with the proposed method.

Applications

The developed method was applied to the quantitative determination of traces of residual chlorine in real matrixes such as tap water, swimming pool water, sewage waste water, lake water and well water. The results listed in TABLE 2, compare favorably with those from the reference method [DPD method]. Statistical analysis of the results by use of Student's t-test and F test showed no significant difference between the accuracy and precision of the proposed and reference method.

Conclusion

The methods do not involve troublesome reaction conditions and can be compared favorably with other methods. Although a variety of methods are available for the determination of residual chlorine, the developed method is simple, inexpensive, sensitive and precise and have the advantage of determinations without the need for extraction or heating and reaction time is about 20min for the assay. Thus they can be used as alternative to present methods for routine analysis. Use of this method for the determination of residual chlorine in variety of real samples has demonstrated its utility.

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