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Extractive liquid–liquid spectrophotometric procedure for the determination of thiocyanate ions employing the ion pair reagent amiloride monohydrochloride

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Abstract

An accurate, inexpensive and less laborious liquid–liquid extractive spectrophotometric procedure for the determination of thiocyanate ions in aqueous media has been developed. The method has been based upon the formation of a yellow colored complex ion associate of the ion-pairing reagent 1-(3, 5-diamino-6-chloropyrazinecarboxyl) guanidine hydrochloride monohydrate, namely amiloride hydrochloride, $DPG^{+}\cdot Cl^{-}$ and the thiocyanate ions in aqueous media containing HNO_3 (0.5 mol L^{-1}) and subsequent extraction with 4-methyl-2-pentanone. The absorption electronic spectrum of the ion associate showed one well-defined peak at λ_{max} 366 nm. The stoichiometric mole ratio of $DPG^{+}\cdot Cl^{-}$ to the thiocyanate ions is 1:1.The effective molar absorptivity (ε) of the ion associate at λ_{max} 366 nm is $1.1 \pm 0.1 \times 10^4$ L mol^{-1} cm^{-1}. The extraction constants (K_d, K_{ex}, and β) enabled a simple and convenient use of the developed binary ion associate for the extractive spectrophotometric determination of traces of thiocyanate ions in the aqueous media. Beer's law and Ringbom's plots are obeyed in the concentration range 0.05–10 and 0.1–7 μg mL^{-1} of the thiocyanate ions, respectively with a relative standard deviation of ±2.3%. The calculated lower limits of detection (LOD) and quantitation (LOQ) of the developed procedure for the thiocyanate ions were found equal to 0.02 and 0.066 μg mL^{-1}, respectively. The developed method has been applied for the determination of trace amounts of thicyanate ions in tap-, waste- and natural water samples and compared successfully with the reported methods at the 95% confidence level. The proposed method was also applied successfully for the determination of thiocyanate ions in saliva samples.

Keywords: Thiocyanate determination; Chemical equilibrium; Amiloride hydrochloride; Solvent extraction; Spectrophotometry; Wastewater and biological samples

1. Introduction

Thiocyanate ions are present in low concentrations in human serum saliva and in urine. If the content of the thiocyanate ions is a little higher in the body than normal, the protein dialysis will be affected and it may even result in coma [1]. The major cyanide sources in daily human activity are the inhaled smoke by cigarette smokers, causing an increase in thiocyanate levels in human fluids [1]. The toxicity of thiocyanate is significantly less than that of cyanide; however, chronically elevated levels of thiocyanate can inhibit the uptake of iodine by the thyroid gland reducing the formation of thyroxin [2]. The concentration of thiocyanate of human saliva is considered as a biomarker for distinguishing smoking from non-smoking individuals [3]. Saliva thiocyanate may also have an antibacterial role in the mouth, decreasing the corrosion potential of amalgams [3,4]. It is well known that the presence of thiocyanate ions has some relation to local goiter [5–7].

Many spectrophotometric methods based on the formation of the red iron(III)–thicyanate complex have been reported for the determination of thiocyanate [8,9]. The photometric method for NCS^{-} determination was based upon the formation of yellow colored charge-transfer complex (I_2 NCS^{-}) requires the use of a toxic organic solvent [10]. A method for the determination of trace thiocyanate based on the direct reaction of iodine with 2′, 7′-dichlorofluorescein in acid medium to produce a weakly fluorescent species has been reported [11]. A rapid, simple and low sensitive solvent extraction flow injection spectrophotometric method for the simultaneous determination of cyanide and thiocyanate ions via formation of colored (λ_{max} = 540 nm)

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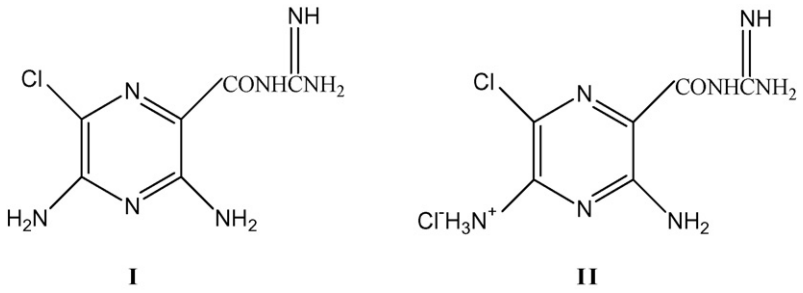

Fig. 1. Chemical structures of amiloride (I) and amiloride hydrochloride (II).

ternary complexes with copper and 2,2′-dipyridyl-2-quinolylhydrazone in chloroform has been reported [12,13]. However, most of these methods suffer from several interferences and are time-consuming [8–10].

The reported ion selective electrodes [14–20] potentiometric methods for the determination of thiocyanate ions were subjected to interferences. Linear sweep polarography [6], liquid chromatography [21], gas chromatography [22] and ion chromatography [23] methods have also been reported. Most of these methods need complicated instrumentation with time-consuming procedures or involve the use of harmful reagents. Due to the urgent need for selective and low cost extraction procedures for the determination of trace amounts of thiocyanate ions, especially in water samples, the present study reports a simple, low cost and precise liquid–liquid extraction spectrophotometric procedure for the complete extraction and subsequent determination of thiocyanate ions in water employing the ion-pair reagent amiloride hydrochloride (Fig. 1). The composition, characterization and chemical equilibrium of the formed complex ion associate were also investigated. The developed method not only separates the thiocyanate ions but also preconcentrate them quantitatively. Thus, the method is also potentially useful for the determination of thiocyanate in biological samples e.g. urine and saliva, where evaluated levels of thiocyanate correlate with excessive cigarette smoking.

2. Experimental

2.1. Reagents and materials

Analytical-reagent grade chemicals and solvents were provided by BDH (BDH Ltd., Poole, England), unless stated otherwise, and were used without further purification. All solutions were made up by doubly de-ionized water. Potassium thiocyanate (Fluka, AG, Buchs, Switzerland) was used for the preparation of stock thiocyanate solution. The reagent amiloride monohydrochloride (E. Merck, Darmstadt, Germany) abbreviated as $DPG^+{\cdot}Cl^-$ was used as received. A stock solution of the reagent $DPG^+{\cdot}Cl^-$ ($0.01\,mol\,L^{-1}$) was prepared by dissolving an accurate weight of the ion-pairing reagent in 100 mL HCl–H_2O (1:1, v/v). A series of Britton–Robinson (B–R) buffer (2.1–10.5) was prepared by mixing equal proportions of acetic acid ($0.08\,mol\,L^{-1}$), phosphoric acid ($0.08\,mol\,L^{-1}$) and boric acid ($0.08\,mol\,L^{-1}$) and adjusting the solution pH to the required value with NaOH ($0.02\,mol\,L^{-1}$) as reported earlier [24].

2.2. Apparatus

A Perkin-Elmer UV/VIS spectrometer (Lambda EZ 150, USA) single beam and a double-beam Perkin-Elmer UV/VIS spectrometer (Lambda EZ 210, USA) with 1 cm (path width) quartz cell (10 mm) were used for recording the absorbance and electronic spectra of the formed complex ion associate. De-ionized water was obtained from Milli-Q Plus system (Milipore, Bedford, MA, USA) was used for preparing all solutions. A pH meter (Orion EA940, MA, USA) was employed for the pH measurements with absolute accuracy limits at the pH measurements being defined by NIST buffers.

2.3. Recommended extraction procedure

In a separating funnel, an aqueous solution (20.0 mL) containing thiocyanate ions ($0.05–10\,\mu g\,NCS^-\,mL^{-1}$) and HNO_3 ($1.0\,mol\,L^{-1}$) was mixed with 2.0 mL of the ion pair reagent $DPG^+{\cdot}Cl^-$ ($2.0\times10^{-3}\,mol\,L^{-1}$) and swirled to mix the contents. The solution was then completed with distilled water to 25 mL and shaken twice with 5 mL (2×2.5) of the 4-methyl-2-pentanone for 2 min. After shaking, the organic extract was then collected in a 25 mL beaker containing anhydrous sodium sulfate (1.0 g), swirled, and transferred to a 25 mL volumetric flask. The residue was also washed with another 5 mL (2×2.5) of the same solvent. The washing solutions and the organic extract were then collected, transferred to the measuring flask (10.0 mL) and finally made up to the mark with the same solvent. The absorbance of the organic extract was then measured at 366 nm against a reagent blank. The concentration of the thoicyanate ions in the aqueous phase before (C_b) and after (C_a) extraction by the developed method was determined by the method reported earlier [9]. The amount of the thiocyanate ions extracted in the organic phase as $DPG^+{\cdot}CNS^-$ was then calculated from the difference ($C_b - C_a$) between the concentration of the thiocyanate ions in the aqueous phase before and after extraction with the reagent $DPG^+{\cdot}Cl^-$. The distribution ratio (D^-_{NCS}) of the thiocyanate ions between the aqueous phase and the organic phase was then calculated employing the equation:

$$D_{NCS} = \frac{[DPG^+ \cdot NCS^-]_{(org)}}{[NCS^-]_{(aq)} + [DPG^+ \cdot NCS^-]_{(aq)}} \quad (1)$$

2.4. Analytical applications

2.4.1. Analysis of thiocyanate in various water samples

2.4.1.1. Direct method. The efficiency of the developed extraction procedure has been studied for the extraction and subsequent determination of traces of thiocyanate ions in various water samples as follows: pipetted 100 mL of the tap- or water samples from water treatment station of Jeddah city, Saudi Arabia were transferred into a 250 mL beaker. To the sample solutions 0.5 mL of NaOH (1.0 mol L^{-1}) and 0.5 mL of EDTA (0.10 mol L^{-1}) were then pipetted into separating funnels (50.0 mL capacity) and centrifuged to remove any formed precipitate. A 2.0 mL concentrated HNO_3 was added to the water sample, filtered through a 0.45 μm cellulose membrane and the pH was then adjusted to zero with the same acid. The thiocyanate ions in the water samples (20.0 mL) after treatment was extracted and analyzed as described in the recommended procedure with the aid of standard curve against a reagent blank as reported [9].

2.4.1.2. Standard addition method. Alternatively, the standard addition (spiking) method was used as follows: a known volume (10 mL) of the water samples after centrifugation in the presence of NaOH (0.5 mL, 1.0 mol L^{-1}) and EDTA (0.5 mL, 0.10 mol L^{-1}), filtrations through a 0.45 μm cellulose membrane and adjustment of the pH to zero with nitric acid (0.5 mol L^{-1}) was spiked with known concentrations (0.05–5 μg mL^{-1}) of thiocyanate ions. The solutions (20.0 mL) were then extracted as described before and the absorbance of the organic extract displayed before and after spiking was measured versus a reagent blank. The change in the absorbance was then used for determining the thiocyanate concentration with the aid of standard addition curve.

2.4.2. Analysis of thiocyanate in biological samples

Human saliva was collected from smoker and non-smoker persons ($n = 5$) following the reported method of Themelis and Tzanavaras in 2002 [8] according to the following procedures: The mouths of the donors were first washed with saliva stimulator (20.0 mL, citric acid 0.5 g w/v) and four times with de-ionized water (4 × 10.0 mL) and stored in low density polyethylene (LDPE) bottles, Nalgene. The collected saliva in LDPE bottles was then shaken in a centrifuge at 2000 rpm for 10 min, filtered through a 0.45 μm filter. The resulting solution was then diluted to 10-fold with de-ionized water and finally the concentration of the thiocyanate ions was determined employing the standard addition method under the optimum experimental conditions of the proposed method.

3. Results and discussion

3.1. Investigation of the various experimental variables

The ion pairing reagent $DPG^+ \cdot Cl^-$ reacts with thiocyanate ions in the aqueous solution in the presence of nitric acid (0.5 mol L^{-1}) to form yellow colored complex ion associate. The produced associate was easily soluble in 4-methyl-2-pentanone. After equilibrium, the organic extract was separated out and its absorption electronic spectrum (Fig. 2) showed one well defined peak maximum at λ_{max} 366 nm ($\varepsilon = 1.1 \pm 0.1 \times 10^4$ L mol^{-1} cm^{-1}) while, in the absence of the thiocyanate ions in the aqueous phase the absorption spectrum of the organic extract of the reagent $DPG^+ \cdot Cl$ showed no peaks in the range of 250–380 nm. The electronic spectrum of the reagent $DPG^+ \cdot Cl^-$ in the aqueous phase showed two well defined peaks at 288 and 354 nm (Fig. 2). In the absence of the potassium thiocyanate or the ion pair reagent $DPG^+ \cdot Cl^-$ in the aqueous phase, no color was observed in the organic phase. In the absence of $DPG^+ \cdot Cl^-$, this observation was also confirmed from the spectrophotometric measurements of the thiocyanate ions in the aqueous phase [9]. Thus, in the subsequent work, the absorbance of the ion associate in the organic extract at 366 nm was used for the spectrophotometric measurements of thiocyanate ions in the aqueous media.

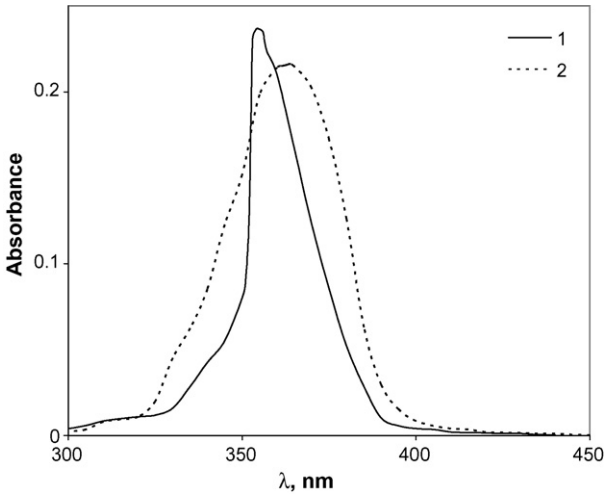

Fig. 2. Electronic spectra of the amiloride hydrochloride (1) in aqueous medium containing nitric acid (0.5 mol mL^{-1}) and the produced complex ion associate of the thiocyanate (1.25 μg mL^{-1}) and the reagent $DPG^+ \cdot Cl^-$ in 4-methyl-2-pentanone (2) against a reagent blank.

The chemical composition of the extracted ion associate of $DPG^+ \cdot Cl^-$ and thiocyanate in 4-methyl-2-pentanone was determined by the Job's continuous variation and molar ratio methods [25]. The data indicated that the ion associate has a thiocyanate to a reagent $DPG^+ \cdot Cl^-$ molar ratio of exactly 1:1. The chemical composition of the produced complex ion associate is a critical parameter, for the sensitivity, the background absorbance and the determination range of the analyte. Mole ratios of 1:1 resulted in a high sensitivity and acceptable background signals due to the formation of the complex ion associate of the general formula $DPG^+ \cdot NCS^-$ which is readily extractable into the organic phase [26]. Based on these results in 4-methyl-2-pentanone and the data reported earlier for the complex ion associates of the reagent $DPG^+ \cdot NCS^-$ with percholarate [27], perrhenate [28], and periodate [29,30], the overall reaction of thiocyanate ions with $DPG^+ \cdot Cl^-$ in HNO_3 (0.5 mol L^{-1}) was most likely proceeded as follows:

$$HCNS \rightleftharpoons H^+ + CNS^- \qquad K = 0.20 \tag{2}$$

$$DPG^+ \cdot Cl^- + CNS^- \rightleftharpoons DPG^+ \cdot CNS^- + Cl^- \tag{3}$$

The effect of pH (0–10.5) upon the reaction of $DPG^+ \cdot Cl^-$ with NCS^- ions in the aqueous phase and subsequent solvent extraction of the produced species employing HNO_3 (0.5 mol L^{-1}) and/or B–R buffer was studied. The concentration of the thiocyanate ions and $DPG^+ \cdot Cl^-$ was fixed at 1×10^{-5} and 1.2×10^{-5} mol L^{-1}, respectively. The final pH of the aqueous solution was adjusted before the extraction and the absorbance of the developed colored extract in 4-methyl pentan-2-one was measured at 366 nm against reagent blank. In the pH range higher than pH 2.5 no extraction was observed, while on lowering the pH ≤ 2.1, the sensitivity and the background absorbance considerably raised and maximum absorbance of the produced complex ion associate was obtained at pH zero. At pH about zero, the thiocyanate ions may exist only as anionic species (NCS^-) depending on the thiocyanate concentration and the ionic strength as reported earlier for periodate anion [29]. Thus, the overall reaction involves formation of the ion associate of the general formula $DPG^+ \cdot NCS^-$. The decrease in the absorbance of the extracted species on raising the pH is most likely due to the formation of non-extractable forms of thiocyanate ions and/or the instability of the complex species formed in the extraction media.

The extraction performance of the complex ion-associate of thiocyanate ions with $DPG^+ \cdot Cl^-$ was investigated in a series of organic solvents namely: *n*-hexane, *n*-heptane, diethyl ether, petroleum ether, dichloromethane, carbon tetrachloride, toluene, chloroform, cyclohexane and 4-methyl-2-pentanone. The extraction followed the sequence: 4-methyl pentan-2-one > diethyl ether > petroleum ether > chloroform > toluene > dichloromethane > *n*-hexane ≃ carbon tetrachloride in agreement to some extent with the order of the dielectric constants of the diluents [32]. Maximum absorbance, apparent molar absorptivity, stability, distribution ratio ($D = 22.7$) and solubility of the produced complex ion associate were achieved in 4-methyl-2-pentanone. Thus, 4-methyl-2-pentanone was selected as the proper organic phase in the subsequent work because (i) the extraction is complete in a very short time; (ii) its lower density allows a better separation of the phases and finally (iii) thiocyanate ions or the ion pair reagent $DPG^+ \cdot Cl^-$ separately are also not extracted into this solvent.

The stability of the produced ion associate depends considerably on the nature of the mineral acid present in the aqueous phase. Thus, the effect of the mineral acids: HCl, H_2SO_4 and HNO_3 at 0.50 mol L^{-1} concentration upon the extraction of the associate of the thiocyanate with the reagent $DPG^+ \cdot Cl^-$ was studied. The data revealed that the nature of the mineral acid contributes substantially to the maximum extraction of the complex ion associate and maximum absorbance of the colored species was obtained in HNO_3 (0.5 mol L^{-1}). In nitric acid (0.5 mol L^{-1}) an excellent extraction percentage (98.6 ± 2.3%) of the thiocyanate ions in the organic phase was achieved as indicated from the determination of thiocyante remained in the aqueous phase [9]. The absorbance value of the colored associate in the organic phase followed the sequence:

$$HNO_3 > HCl > H_2SO_4 \quad (4)$$

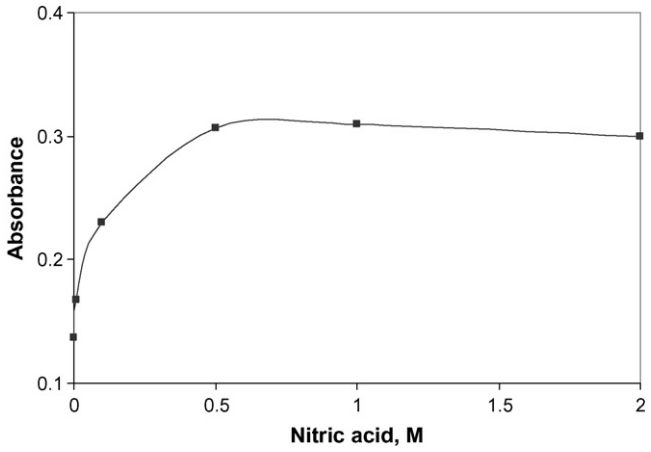

Fig. 3. Influence of HNO_3 concentration (0.1–2 mol L^{-1}) on the extraction of the ion associate of thiocyanate–$DPG^+ \cdot Cl^-$ into 4-methyl-2-pentanone against a reagent blank.

The data indicated that the stability of the binary ion associate is higher in HNO_3. Thus, the influence of HNO_3 concentration (0.1–4 mol L^{-1}) on the formation of $DPG^+ \cdot NCS^-$ and subsequent solvent extraction of the ion associate of thiocyanate was investigated. Maximum extraction was achieved at acid concentration >0.5 mol L^{-1} of the aqueous phase (Fig. 3). Thus in the subsequent work, nitric acid (0.5 mol L^{-1}) was used as the preferable extraction medium.

The effect of shaking time on the extraction of the complex ion associate $DPG^+ \cdot NCS^-$ with 4-methyl-2-pentanone at different time intervals ranging from 30 s to 5 min was investigated. The extraction was rapid and maximum absorbance was achieved at 2 min shaking time or more and hence a 2 min shaking time was adopted in the subsequent work. The developed ion associate was stable for up to 3 h for samples containing ≤10 μg mL^{-1} of thiocyanate in the aqueous solution at pH zero containing HNO_3 (0.50 mol L^{-1}).

The influence of the reagent $DPG^+ \cdot Cl^-$ concentration (1.0×10^{-5}–2.0×10^{-3} mol L^{-1}) on the solvent extraction of the ion associate at the optimum experimental conditions was studied. The use of 2 mL of 2.0×10^{-3} mol L^{-1} $DPG^+ \cdot Cl^-$ solution was found sufficient for complete extraction of up to 10 μg mL^{-1} thiocyanate ions in the aqueous phase (20 mL). Accordingly, 2.0 mL of 2.0×10^{-3} mol L^{-1} of $DPG^+ \cdot Cl^-$ solution was added in all further experiments. The absorbance of the organic extract $DPG^+ \cdot NCS^-$ increased linearly on increasing the thiocyanate concentration up to 10 μg mL^{-1} in the aqueous phase at the optimum ion-pair concentration (2.0 mL, 2.0×10^{-4} mol L^{-1} $DPG^+ \cdot Cl^-$).

3.2. Interference study

The developed method has been applied for the extraction of 2.5 μg mL^{-1} of the thiocyanate ions in the presence of a relatively high excess (0.05–0.1 mg mL^{-1}) of the diverse ions: Ca^{2+}, NH_4^+, Al^{3+}, Fe^{2+}, $AuCl_4^-$, the base metal ions e.g. Ni^{2+}, $Cu^{2+}$and Zn^{2+} and the anions: Cl^-, Br^-, SO_4^{2-}, CO_3^{2-}, $C_2O_4^{2-}$, PO_4^{3-} and $S_2O_8^{2-}$. The tolerance limit was

defined as the concentration of the foreign ion added causing a relative deviation within ±2% of the recovery of the thiocyanate ions. The ions: Fe^{3+}, Co^{2+}, VO_3^- and MnO_4^- interfered seriously even at low concentrations while the other ions did not interfere at 1:100 tolerable concentration of thiocyanate to the diverse ions. The interference of MnO_4^- was minimized to 1:25 by the addition of few drops of NaN_3 (0.1%, w/v) prior to their extraction. The interference of the ions VO_3^- and MnO_4^- is most likely attributed to the ability of these ions to form extractable stable complex ion associates with the reagent $DPG^+{\cdot}Cl^-$ in the organic phase. On the other hand, the interference of the ions Co^{2+}, VO_3^- and Fe^{3+} is possibly attributed to the ability of these ions to form extractable complexes with the thiocyanate ions in the aqueous phase and subsequently extracted onto the organic phase. The interference of the ions VO_3^-, Co^{2+} and Fe^{3+} was successfully eliminated by the addition of few drops of NaF (1%, w/v) or EDTA (0.5 mL, 0.10 mol L^{-1}). Hence, in the subsequent work of the developed method EDTA (0.5 mL, 0.10 mol L^{-1}) solution was added to mask the possible interference by the ions Fe^{3+}, Co^{2+}, VO_3^-, Cr^{3+} on the determination of thiocyanate ions in various water samples.

3.3. Extraction equilibrium in the model system

Assuming that there is no dimerization of the extracted species and the formation of poly anion ion associates is negligible, the equilibrium constants K_{ex}, β and K_d of the system containing thiocyante ions and the reagent $DPG^+{\cdot}Cl^-$ and the solvents (water and 4-methyl-2-pentanone) at pH zero using HNO_3 (0.50 mol L^{-1}) have been calculated employing the following extraction equilibrium [31,33]:

(i) Formation of the ion associate proceeded at pH 5–9 according to the equation:

$$NCS^-_{(aq)} + DPG^+_{(aq)} \rightleftharpoons [DPG^+ \cdot NCS^-]_{(aq)} \quad (5)$$

with a corresponding ion associate equilibrium constant, β

$$\beta = \frac{[DPG^+ \cdot NCS^-]_{(aq)}}{[NCS^-]_{(aq)}[DPG^+]_{(aq)}} \quad (6)$$

(ii) Distribution of the complex ion associate between the aqueous and the organic phase with a corresponding distribution coefficient, K_d

$$[DPG^+ \cdot NCS^-]_{(aq)} \rightleftharpoons [DPG^+ \cdot NCS^-]_{(org)} \quad (7)$$

$$K_d = \frac{[DPG^+ \cdot NCS^-]_{(org)}}{[DPG^+ \cdot NCS^-]_{(aq)}} \quad (8)$$

(iii) The overall extraction process is then described by the equation:

$$NCS^-_{(aq)} + DPG^+_{(aq)} \rightleftharpoons [DPG^+ \cdot NCS^-]_{(org)} \quad (9)$$

With the corresponding equilibrium constant, which is often called extraction constant, K_{ex}, is given by the equation:

$$K_{ex} = \frac{[DPG^+ \cdot NCS^-]_{(org)}}{[DPG^+]_{(aq)}[NCS^-]_{(aq)}} = K_d\beta \quad (10)$$

Taking into consideration that only one complex species of thiocyanate ions is present in the aqueous phase i.e. $NCS_{(aq)}^-$ is the only predominant species at the given pH. Thus, the distribution ratio, D_{NCS} takes the following:

$$D_{NCS} = \frac{\sum [NCS^-]_{(org)}}{\sum [NCS^-]_{(aq)}} \quad (11)$$

$$D_{NCS} = \frac{[DPG^+ \cdot NCS^-]_{(org)}}{[NCS^-]_{(aq)} + [DPG^+ \cdot NCS^-]_{(aq)}} \quad (12)$$

Assuming that at low concentrations of the reagent $DPG^+{\cdot}Cl^-$ i.e. $[NCS^-] \ggg [DPG^+{\cdot}Cl^-]$, the association in the aqueous phase $[DPG^+{\cdot}NCS^-]_{(aq)}$ is negligible. Thus, the term $[DPG^+{\cdot}NCS^-]_{(aq)}$ can be neglected in Eq. (12). Therefore, Eq. (12) transforms into:

$$D_{NCS} = \frac{[DPG^+ \cdot NCS^-]_{(org)}}{[NCS^-]_{(aq)}} \quad (13)$$

After substituting Eq. (13) into Eq. (10) and taking logarithms, the following Eq. (14) is then obtained:

$$\log D_{NCS} = \log K_d\beta + \log [DPG^+]_{(aq)} \quad (14)$$

The D values at the initial concentration of NCS^- (2.5 μg mL^{-1}) in the aqueous phase of pH zero and various concentrations (1.0×10^{-5}–40.0×10^{-5} mol L^{-1}) of the reagent $DPG^+{\cdot}Cl^-$ were then calculated. The values of β, K_{ex} and K_d of the extracted ion associate were then determined graphically from the linear plot of log D_{NCS}^- versus log $[DPG^+{\cdot}Cl^-]$ (Fig. 4). A slope of 0.8 was obtained confirming the formation of complex ion associate of 1:1 molar ratios of thiocyanate ions to the reagent $DPG^+{\cdot}Cl^-$, respectively. The low value of

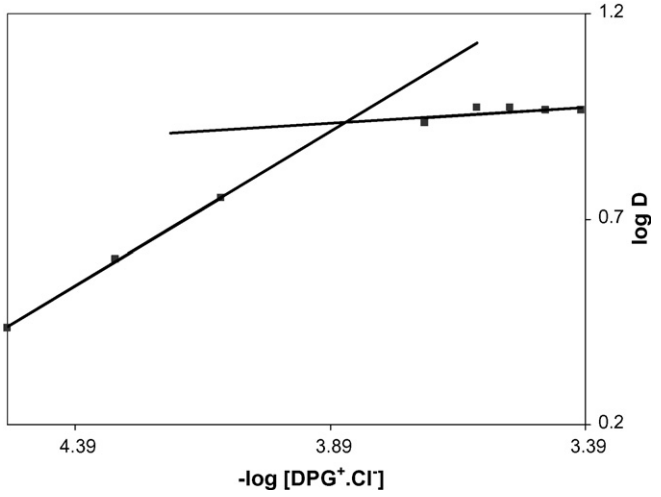

Fig. 4. Plot of log $DPG^+{\cdot}Cl^-$ versus log D of the extracted ion associate $DPG^+{\cdot}NCS^-$ into 4-methyl-2-pentanone from aqueous media containing HNO_3 (1.0 mol mL^{-1}) against a reagent blank.

the slope than the expected value (1.0) is most likely attributed to the possible interference of HNCS in the extraction step under the experimental conditions employed. However, these data added further support for the existence of the complex ion associate $DPG^+{\cdot}NCS^-$ and the absence of non-specific interaction between the extracted complex ion associate $DPG^+{\cdot}NCS^-$ and the ion-pair reagent $DPG^+{\cdot}Cl^-$ [29]. The data are excellent and are in good agreement with the results obtained from the Job's continuous variation [25]. Therefore, the most probable composition of the extracted species is $DPG^+{\cdot}NCS^-$. At high concentrations of the reagent $DPG^+ \cdot Cl^-_{(aq)}$, the respective term $[NCS^-]_{(aq)}$ be was neglected. Therefore, Eq. (12) takes the form of Eq. (8) i.e $D_{NCS} = K_d$. Thus, at high concentration of the $DPG^+{\cdot}Cl^-$, the plot of the experimental data of log D versus log $DPG^+{\cdot}Cl^-$ in the same coordinates according to Eq. (8) was linear and slightly parallel to the abscissa with a slope of 0.07 (Fig. 4). The K_d value was then calculated from the intercept of log D axis of the plot. Thereafter using Eq. (10), the value of β was then calculated. The K_{ex}, K_d and β values calculated from Fig. 4 were found equal to $2.07 \pm 0.\ 2 \times 10^4$, 22.1 ± 0.7 and $1.96 \pm 0.25 \times 10^3$, respectively.

3.4. Photometric characteristics and analytical performance

After adjusting the experimental conditions of the reagent $DPG^+{\cdot}Cl^-$, extraction media and the thiocyanate ions, a linear graph on recording the absorbance at 366 nm versus thiocyanate concentration (0.1–20 μg mL^{-1}) was obtained. Beer's law is obeyed in the concentration range 0.1–10 μg mL^{-1}.The molar absorptivity calculated from Beer-Lambert's plot and Sandell's sensitivity index [34,35] of the complex ion associate at 366 nm were estimated to be $1.1 \pm 0.1 \times 10^4$ L mol^{-1} cm^{-1} and 0.08 μg cm^{-2}, respectively. The effective concentration range of thiocyanate ions as evaluated by Ringbom's plot [36] is obeyed in the range 0.1–7 μg mL^{-1} μg mL^{-1}. The relative standard deviation (S_r) of five measurements with 5 μg mL^{-1} of thiocyanate was estimated as 2.2%. The lower limits of detection (LOD) and quantitation (LOQ) under the conditions established for thicyanate ions were estimated using the equations [37].

$$\mathrm{LOD} = \frac{3\delta}{b} \tag{15}$$

and

$$\mathrm{LOQ} = \frac{10\delta}{b} \tag{16}$$

where δ is the standard deviation ($n = 5$) of the blank and b is the slope of the calibration plot.. The lower limits of detection (LOD) and quantitation (LOQ) of the developed procedure are 0.02 and 0.066 μg mL^{-1} thiocyanate. Such limits could be improved to lower values on increasing the volume of the aqueous phase containing traces of thiocyanate and amiloride at the optimum experimental condition, which will be shaken with the organic solvent. The results were compared successfully with the reported method [9], in terms of the detection limit (3δ), range of linearity and precision. The linear range and the time consumption of the developed method are also better than the reported spectrophotometric methods [8–10].

3.5. Analytical applications

3.5.1. Determination of thiocyanate in various water samples

The values of the effective molar absorptivity (ε) of the Beer-Lambert's plot and the values of the extraction constants (K_{ex}, $K_{d,}$ β and D) of thiocyanate ions of the proposed extraction system have suggested the use of the developed procedure conveniently for thiocyanate determination in various water samples. The water samples were analyzed by the direct method following the recommended extraction procedures described earlier with the aid of calibration curve. The results showed the absence of thiocyanate ions in the tested water samples and are in good agreement with the iron(III)–thiocyanate method [9]. Alternatively, the standard addition method was also applied at various concentrations of the thiocyanate (2.5.0–10.0 μg NCS^- mL^{-1}) spiked to water samples. A satisfactory recovery percentage (97–104 ± 2.4%) of the thiocyanate ions spiked to the seawater samples at the employed concentration was achieved (Table 1) in the presence of EDTA as mentioned in Section 2.4 to prevent the possible interference caused by iron(III), chromium(III) and bismuth(III). The developed extraction procedure was also tested for the separation and spectrophotmetric determination of traces of thiocyanate species spiked to the industrial wastewater samples. Thiocyanate ions at a total concentration ≤10 μg mL^{-1} were spiked into the wastewater samples as described in Section 2. The data summarized in Table 2 are in good agreement with the results reported obtained via iron(III)–thiocyanate method [9] with an acceptable recovery percentage (97 ± 2.5%, $n = 5$). The F- and t-tests at 95% confidence levels did not exceed the tabulated (theoretical) ones and no significant differences were observed between the developed and the reference methods [9] with respect to precision and accuracy. Thus, statistical analysis revealed that the developed method is good and applicable with the reported method.

3.5.2. Determination of thiocyanate in biological samples

The validity of the developed method was also tested by the determination of the thiocyanate ions in biological samples e.g. human saliva of cigarette smoker and non-smoker members by the standard addition method. The saliva and urine sam-

Table 1
Determination of thiocyanate ions (2.5–10 μg mL^{-1}) spiked to seawater samples (20 mL) by the developed procedure (A) and reference spectrophotometric [9] method (B)[a]

Thiocyanate (μg mL^{-1})			Recovery (%)[a]	
Added	Found		A	B
	A	B		
2.5	2.6	2.5	104.0 ± 2.7	100.0 ± 2.1
5.0	5.1	5.15	102.0 ± 2.3	103. ± 2.2
10	9.7	10.2	97.0 ± 2.3	102.0 ± 2.2

[a] Average of five measurements ± standard deviation.

Table 2
Determination of thiocyanate ions (0.05–10 μg mL^{-1}) spiked to wastewater samples (20.0 mL) by the developed procedure (A) and reference spectrophotometric [9] method (B)[a]

Thiocyanate (μg mL^{-1})			Recovery (%)[a]	
Added	Found		A	B
	A	B		
0.05	0.052	0.053	104.0 ± 1.7	106.0 ± 1.8
0.5	0.52	0.51	104.0 ± 2.1	101.0 ± 2.7
2.5	2.4	2.4	96.0 ± 2.3	96.0 ± 3.1
5.0	4.9	5.1	98 ± 1.9	102.3 ± 2.6
10	9.8	10.1	98 ± 2.1	101 ± 1.7

[a] Average of five measurements ± standard deviation.

Table 3
Determination of thiocyanate ions (0.05–0.5 μg mL^{-1}) spiked to human saliva (20 mL) by the developed procedure (A) and standard colorimetric [38] method (B)[a]

Thiocyanate, μg mL^{-1}		
Added	Found	
	A	B
Saliva of non-smokers		
0.05	0.57 ± 0.05	0.60 ± 0.03
0.5	1.1 ± 0.04	1.2 ± 0.02
Saliva of smokers		
0.05	2.2 ± 0.09	2.30 ± 0.10
0.5	2.9 ± 0.15	3.1 ± 0.2

[a] Average of five measurements ± standard deviation.

ples ($n = 5$) were prepared and treated as reported earlier [8] in Section 2. The samples were then analyzed by the standard addition method under the optimum experimental conditions. The results (Table 3) are compared with the reference colorimetric method [38]. The data obtained by the developed method for the thiocyanate determination are in good agreement with those obtained via the standard colorimetric method [38] reflecting the utility of the proposed spectrophotometric procedures.

4. Conclusions

The method is simple, rapid, free from systematic errors, low cost and provides reliable procedures for the determination of thiocyanate ions in water samples at low level. The method is less laborious than the conventional method and has a similar precision to that of the conventional ones [9,38,39]. The molar absorptivity of the developed ion associate reaches $1.1 \pm 0.1 \times 10^4$ L mol^{-1} cm^{-1}. Most foreign ions do not interfere with the determination of thiocyanate ions. The developed method has been shown to have good operating characteristics (sensitivity, stability, time consuming, detection limit, and a wide linear range). The method can be used for determination of thiocyanate ion in biological samples. The photometric and extractive characteristics make the use of the developed method attractive and convenient for routine control determination of thiocyanate ions. However, work is continuing for the application of online flow injection analysis for the routine determination of thiocyanate and complexes of metal ions containing thiocyanate.

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