

Research Article

Development of Flow Injection Spectrophotometric Method for 1-Naphthylthiourea Using Sodium Nitrite and Sulphanilic Acid Diazotization Reaction

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A simple spectrophotometric method in conjunction with flow injection analysis is developed for the quantitative analysis of 1-naphthylthiourea (ANTU). The reaction is based on the alkaline hydrolysis of ANTU to 1-naphthylamine at 30°C, coupled with diazotized sulphanilic acid resulting in 4-(sulphophenylazo)-1-naphthylamine which is monitored at 495 nm. The limit of detection ($S/N=3$) is 0.01 mg/L with a sampling throughput of 45/h. The method is linear over the range of 0.05–120 mg/L ($R^2 = 0.9995$, $n = 7$), with calibration equation $y = 0.031x - 0.018$ ($y =$ absorbance; $x =$ mg/L) and relative standard deviation ($n = 3$) 1.8–3.6%. Experimental variables are optimised, and the interfering effects of different pesticides, organic compounds, cations, and anions at environmentally relevant concentrations are investigated. The analysis of ANTU in spiked water samples is extracted with solid phase procedure using disposable Sep-Pak C18 cartridges, and the recovery was 93 ± 1.9 – $110 \pm 3.0\%$. The results of the proposed method are compared with the HPLC method by applying the F -test and paired Student t -test at 95% confidence level.

1. Introduction

1-Naphthylthiourea (ANTU) is a rodenticide that belongs to the class of organosulfur pesticide and available in the form of white crystalline powder [1–4]. It is used as 10% active baits or 20% tracking powder [5]. It is specifically used to control adult *Rattus norvegicus*, and 6–8 mg/kg is sufficient as a toxic dose; however, other species of *Rattus* are less toxic to it. The repetitive administration of rates with its sublethal doses develops tolerance [6]. In general, domestic animals are safe from its toxic effects, but the induction of vomiting in dogs and production of pleural effusion and pulmonary oedema in other experimental animals have been reported [7].

Human exposure to ANTU could be through ingestion, inhalation, or skin contact with the recommended occupational airborne exposure over an average of a ten-hour work shift is 0.3 mg/m^3 , while an exposure of 100 mg/m^3 has been reported

to be dangerous for human health [3]. A 4000 mg-ANTU/kg human body weight has been assigned as a lethal dose [8]. It does not degrade in the presence of sunlight and air. 1-naphthylamine can cause coughing, breath shortness, or fluid buildup in the lungs. It is the main degraded product of ANTU and is considered to be a first-class carcinogen, which can easily enter the fluvial systems in different ways [8, 9]. The chemical structure of ANTU is shown in Figure 1.

Various analytical procedures have been employed for the determination of ANTU in biological, food, and environmental samples. These include colorimetry [10, 11], fluorimetry [12], voltammetry [13, 14], liquid chromatography based on different detectors [15–18], and stop flow injection chemiluminescence [19]. They are accurate and sensitive, however, require large amount of reagents, lengthy procedures, low sample throughputs, and expertise. Spectrophotometry continues to gain popularity due to simplicity, speed, precision,

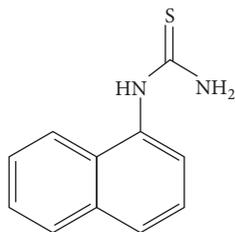


FIGURE 1: Chemical structure of ANTU (α -naphthylthiourea).

accuracy, and availability of instrumentation. The flow injection analysis (FIA) is well established for the analysis of diverse analytes in the environmental, clinical, food, and other areas. It has the advantages of high injections throughput, low sample and reagent consumption, and high versatility and robustness. In particular, spectrophotometry has become the most widely used detection technique in FIA [20].

This study reports a simple FI spectrophotometric method for the determination of ANTU in natural waters, based on the conversion of nitrite into nitrous acid, subsequent diazotization of sulphanilic acid, and formation of the diazonium salt. The diazonium salt is coupled with 1-naphthylamine, the hydrolysed product of ANTU under alkaline conditions to form 4-(sulphophenylazo)-1-naphthylamine [9, 21]. The azo dye formed is monitored at 495 nm. The interfering effects of different pesticides, organic compounds, cations, and anions have also been investigated. ANTU from water samples has been extracted using a solid phase extraction technique, analysed by the proposed method, and validated by the HPLC method.

2. Experimental

2.1. Materials and Solutions. All chemicals used were of analytical grade provided by Merck (Darmstadt, Germany) and BDH Chemicals Ltd. (Poole, UK). Glassware and bottles were precleaned in 10% hydrochloric acid for three days, thoroughly rinsed with deionised water (0.067 μ S/cm, Elga Purelab Option, High Wycombe, Bucks, UK) and stored in the zip-locked plastic bags. A 0.1 M stock solution of sulphanilic acid was freshly prepared by dissolving 4.33 g in deionised water, sonicated for 5 min, diluted to 250 mL with deionised water, and stored in a dark brown bottle. A 0.25 M stock solution of sodium nitrite was prepared by dissolving 4.3 g in deionised water, and the volume was made up to 250 mL with deionised water. A 2.0 M stock solution of sodium hydroxide was prepared by dissolving 8.0 g in deionised water, and the volume was made up to 100 mL with deionised water. Working standard solutions were prepared from these stock solutions in deionised water when required. Commercially available absolute ethanol was used for making different ethanol working standard solutions (% v/v) with deionised water.

For the preparation of 250 mg/L stock solutions of ANTU, asulam, diazinon, malathion, maneb, nabam, phoxim, terbufos, thiabendazole, and thiram (Dr. Ehrenstorfer, Augsburg, Germany), the preweighed amounts of these pesticides were dissolved in absolute ethanol. All these solutions were

sonicated and stored in dark brown bottles at 4°C when not in use. These solutions were diluted serially to obtain lower concentrations using 0.25% (v/v) ethanol solution containing 75 mM sodium hydroxide.

For the preparation of 2000 mg/L stock solutions of cations, such as sodium, potassium, magnesium, calcium, iron, manganese, and cobalt, and anions, such as chloride, nitrate, sulphate, and phosphate, the required quantities of related salts were dissolved in deionised water and the working standard solutions were prepared in 0.25% ethanol solution containing 75 mM sodium hydroxide.

2.2. Flow Injection Manifold. The proposed three-channel FI manifold is shown in Figure 2. All the streams were propelled at a flow rate of 0.5 mL/min by using a 4-channel peristaltic pump (Reglo 100, Glattbrugg-Zurich, Switzerland). The standards and samples of ANTU (300 μ L) were injected via a rotary injection valve (Rheodyne 5020, Anachem, Luton, UK) into the carrier stream of 0.25% (v/v) ethanol solution containing 75 mM sodium hydroxide, which resulted in the formation of 1-naphthylamine. For diazonium salt formation, the streams of 100 mM sulphanilic acid and 50 mM sodium nitrite were merged at a T-piece and allowed to pass through a 200 cm reaction coil-I, thermostated at 30°C. This stream was then merged with the carrier stream containing 1-naphthylamine at a confluence point and passed through 150 cm reaction coil-II which was also thermostated at 30°C. This resulted in the formation of 4-(sulphophenylazo)-1-naphthylamine monitored at 495 nm using a UV-Vis spectrophotometer (Model 6505, Jenway Ltd., Feisted, Dunmow, Essex, UK) and equipped with a quartz flow-through cell (path length 1 cm, volume 80 μ L, Hellma Analytics, Germany). The absorbance was recorded on a chart recorder (BD40, Kipp & Zonen, Delft, Netherlands). Polytetrafluoroethylene tubes (0.8 mm i.d., Fisher Scientific, Loughborough, UK) were used to join all connections of FIA manifold.

2.3. Water Samples Collection. Natural water samples such as tap, irrigation, and lake water from Quetta valley were collected in 10% hydrochloric acid, washed in high-density polyethylene bottles, and stored in the dark at 4°C. For the removal of suspended solids, water samples were filtered through a cellulose membrane filter (diameter 47 mm; pore size 0.45 mm), (Whatman, Madistone, UK), stored at 4°C, and analysed when required.

The water samples were spiked with ANTU in the range from 0.5 to 3.0 mg/L and extracted with solid phase extraction (SPE) using disposable Sep-Pak C18 cartridges (Water Associates, USA). The cartridge was first conditioned with 5.0 mL deionised water, 5 mL ethanol, and then dried by passing air through it for two minutes. The water sample was passed at a flow rate of 10 mL/min through the conditioned SPE cartridge, washed with 0.5 mL deionised water, and dried by passing air through it for 10 min. ANTU from the SPE cartridge was eluted with 5.0 mL ethanol and dried under a nitrogen stream. The dried ANTU residues were redissolved in 0.25% ethanol containing 75 mM sodium

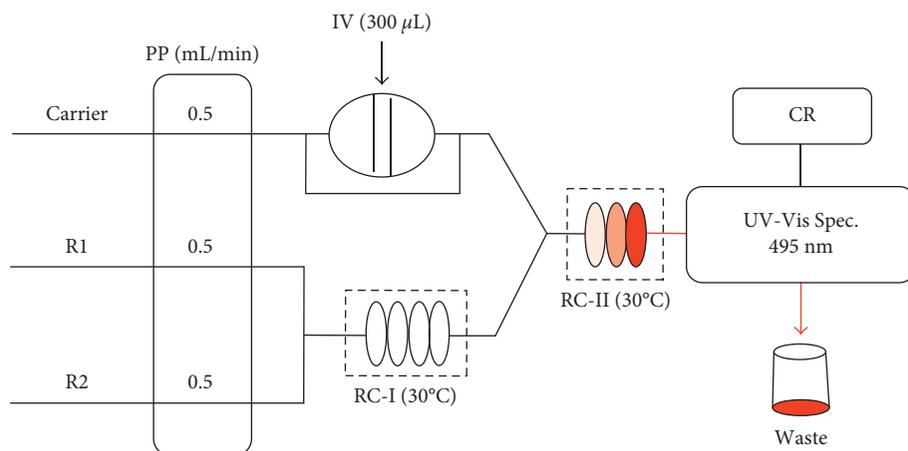


FIGURE 2: Optimised FI spectrophotometric manifold for the determination of ANTU. Carrier, 0.25% (v/v) ethanol solution containing 75 mM sodium hydroxide; R1, 50 mM sodium nitrite solution; R2, 100 mM sulphanic acid solution; PP, peristaltic pump; IV, injection valve; RC-I, reaction coil-I, 200 cm; RC-II, reaction coil-II, 150 cm; CR, chart recorder.

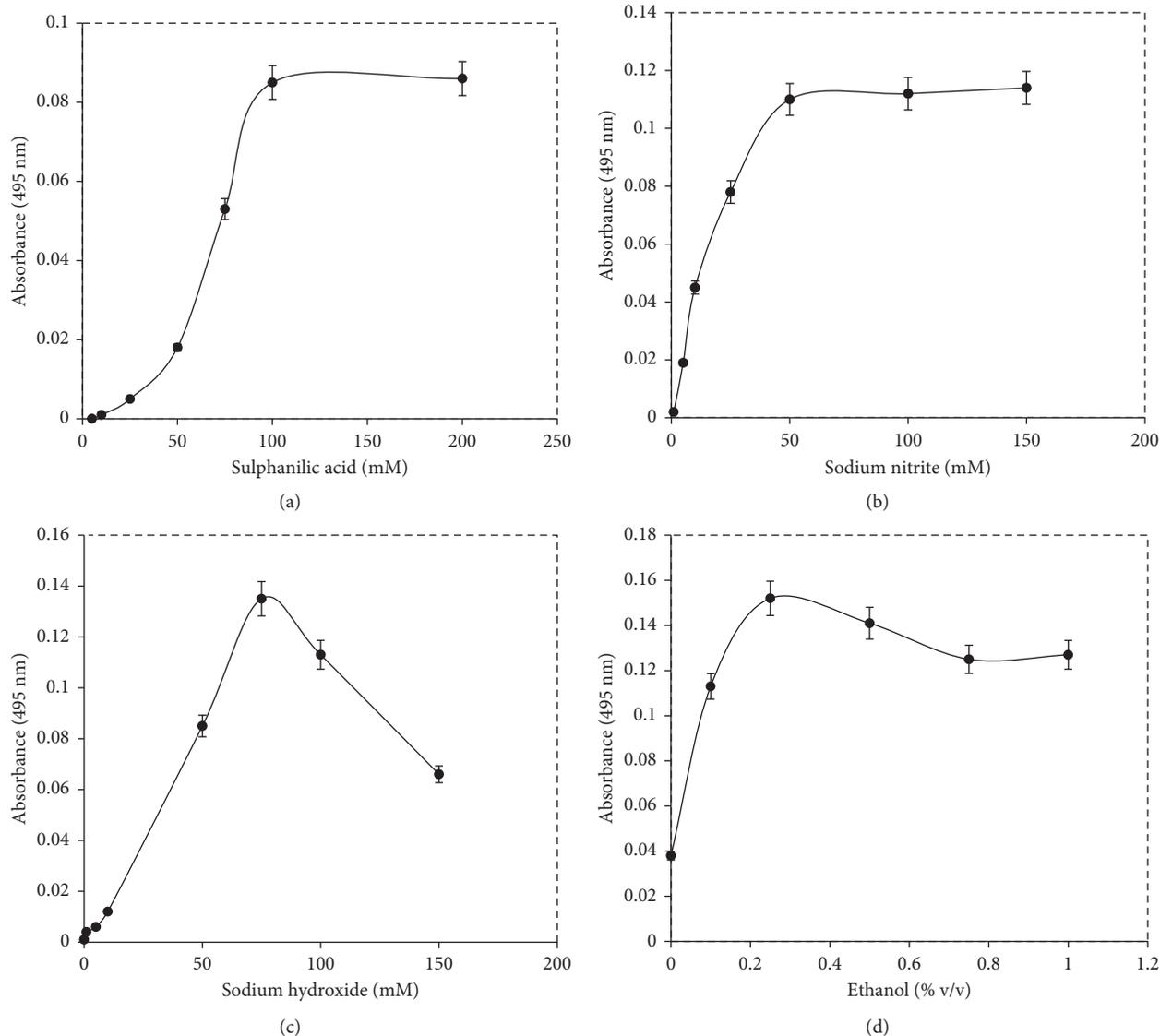


FIGURE 3: Optimization of reagents concentration. (a) Sulphanilic acid, (b) sodium nitrite, (c) sodium hydroxide, and (d) ethanol. Experimental conditions: flow rate 0.5 mL/min, sample loop volume 300 μ L, reaction coil-I length 200 cm, reaction coil-II length 150 cm, wavelength 495 nm, temperature 30°C, and ANTU concentration 10 mg/L.

TABLE 1: Effect of physical variables on the determination of ANTU ($n = 4$).

Physical variables	Range studied	Optimum
Flow rate (mL/min)	0.2–1.2	0.5
Sample injection volume (μL)	60–360	300
Reaction coil-I length (cm)	0–300	200
Reaction coil-II length (cm)	0–300	150
Reaction coil-I and -II temperature ($^{\circ}\text{C}$)	10–50	30

hydroxide and 0.1% acetic acid-acetonitrile (55 : 45, v/v), and both were analysed by the proposed method and a previously reported HPLC method [15], respectively.

2.4. HPLC Method. The ANTU standards and samples were analysed by the HPLC method as reported previously [15]. In brief, a liquid chromatograph (Model LC-10AT, Shimadzu, Corporation, Tokyo, Japan) equipped with a UV-Vis detector (SPD-10A) set at 220 nm was employed. The samples were introduced through a six port injection valve (Model 7725i, Rheodyne) with a sample loop volume of 10 μL . The chromatographic analysis was performed on an analytical column (Bondapak C18: 250 \times 4.6 mm i.d., 10 μm) using 0.1% acetic acid-acetonitrile (55 : 45, v/v) as a mobile phase at a flow rate of 2 mL/min. Under these conditions, the retention time for ANTU was 2.1 min while a linear calibration graph was obtained by injecting the analyte standard solutions over the range 0.1–5 mg/L. The residues of analyte after SPE were dissolved in the mobile phase and analysed by the method.

3. Results and Discussion

3.1. Experimental Results. Various analytical parameters were optimised to enhance the sensitivity, increase the dynamic linear range and sample throughput, and reduce reagents consumption. All these studies were performed with 10 mg/L ANTU standard solution.

The spectrum of the final product of the reaction (Scheme 3) under the optimum conditions was scanned from 200 to 600 nm. The maximum absorption wavelength of 495 nm was selected as an optimum wavelength for subsequent experiments in the flow mode.

The effect of sulphanic acid concentration in the range of 0.5–200 mM was examined. At 0.5 mM concentration, no absorbance was observed; however, when the sulphanic acid concentration was increased, the absorbance increased linearly. The maximum absorbance was observed at 100 mM sulphanic acid concentration as shown in Figure 3(a). Beyond this concentration, the absorbance remained constant, and bubbles were observed in reaction coil-II due to nitrogen gas generation as a result of the degradation of the diazonium ion. Moreover, the maximum solubility of sulphanic acid concentration (85 mM) at 30 $^{\circ}\text{C}$ was reported [22]. Therefore, the optimum sulphanic acid concentration of 100 mM was selected and used for subsequent studies.

Sodium nitrite was used to generate nitrous acid in acidic medium, and its effect was examined in the concentration

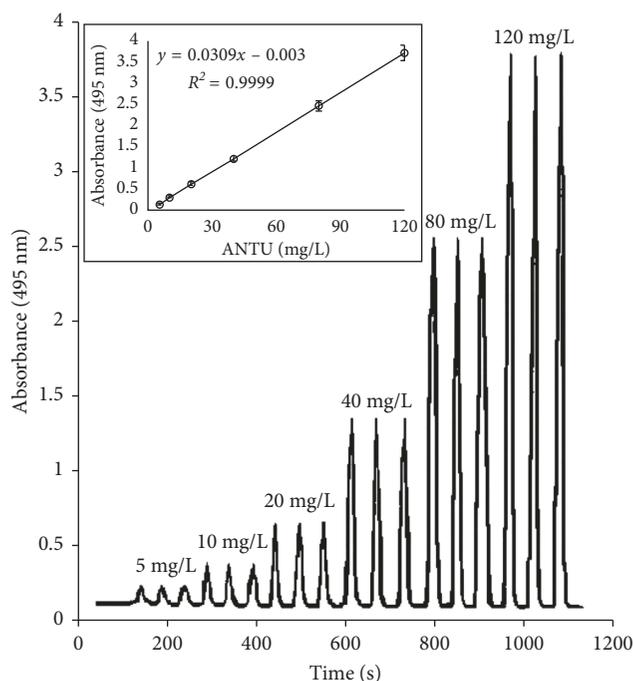


FIGURE 4: Traces of absorbance peak height for a series of ANTU standards injected in triplicate (inset shows the calibration curve).

range of 1–150 mM. Maximum absorbance was obtained at 50 mM as shown in Figure 3(b). Further increase in the sodium nitrite concentration had shown no appreciable increase in the absorbance; therefore, sodium nitrite concentration of 50 mM was selected and used for further studies.

Sodium hydroxide was used to hydrolyse ANTU into 1-naphthylamine [12] and also as a reaction medium for the proposed chemistry. The effect of sodium hydroxide concentration in the range 1–150 mM was examined. Maximum absorbance was observed at 75 mM; above which, the absorbance was decreased as shown in Figure 3(c). Therefore, the sodium hydroxide concentration of 75 mM with a waste (combined stream) of pH 10 was chosen for further studies.

The solubility of ANTU in water has been reported as about 600 mg/L, while in organic solvents, it has the solubility of, for example, 24300 and 86000 mg/L in acetone and triethyleneglycol, respectively [2]. Hence, the effect of ethanol in the range 0–1% (v/v) was examined as a sample carrier stream. The absorbance was increased with an increase in ethanol concentration up to 0.25% above which the peak height absorbance was decreased as shown in Figure 3(d). Therefore, ethanol concentration of 0.25% was selected and used as a sample carrier stream.

To achieve high sensitivity, linear calibration range, and economy of reagents consumption, the effects of various physical parameters such as reagent streams flow rates, sample loop volume, reaction coil lengths, and temperature were examined (Table 1). The effect of flow rates for each of the three streams in the range 0.2–1.2 mL/min was examined simultaneously. Maximum absorbance was observed at 0.5 mL/min with a steady baseline and reproducible peak height;

TABLE 2: Comparison of analytical characteristics of the proposed method with other methods used for the analysis of ANTU.

Technique	Sample matrix	Linear range (mg/L)	LOD (mg/L)	R^2	Reference
FL ^a	Wheat grain	0.05–1.00	0.01	0.999	[12]
DPP ^b	Urine	0.2–10	0.04	—	[13]
ASV ^c	Cattle feed and urine	Up to 0.81	8×10^{-5}	0.9980	[14]
HPLC-DAD ^d	River water	—	1.2×10^{-3}	0.9978	[15]
HPLC-MS ^e	Water	2×10^{-4} – 2.5×10^{-2}	9.57×10^{-4}	—	[16]
sFI-CL ^f	Water, wheat, barley, and oat grain	0.05–3	0.005	0.998	[19]
FI spectrophotometry	Water	0.05–120	0.01	0.9995	This work

^aFlourimetry; ^bdifferential pulse polarography; ^cadsorptive stripping voltammetry; ^dhigh-performance liquid chromatography-diode array detector; ^ehigh-performance liquid chromatography-mass spectrometry; ^fstop flow injection-chemiluminescence.

TABLE 3: Percent recovery of ANTU in spiked natural water samples ($n = 4$).

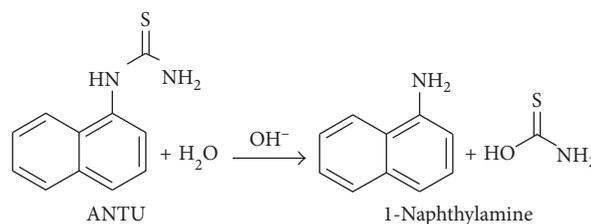
Sample matrix	Spiked (mg/L)	Proposed method		HPLC method [15]	
		Found (mg/L)	Recovered (%)	Found (mg/L)	Recovered (%)
Tap water	0.50	0.49 ± 0.012	98 ± 2.5	0.505 ± 0.011	101 ± 2.2
	1.00	0.93 ± 0.018	93 ± 1.9	1.02 ± 0.032	102 ± 3.1
	1.50	1.44 ± 0.040	96 ± 2.8	1.48 ± 0.027	99 ± 1.8
Irrigation water	1.00	1.03 ± 0.022	103 ± 2.1	1.10 ± 0.033	110 ± 3.0
	2.00	2.09 ± 0.050	105 ± 2.4	1.92 ± 0.063	96 ± 3.3
	3.00	3.12 ± 0.097	104 ± 3.1	2.81 ± 0.048	94 ± 1.7
Lake water	1.00	0.97 ± 0.032	97 ± 3.3	1.06 ± 0.021	106 ± 2.0
	2.00	2.07 ± 0.066	103.5 ± 3.2	1.96 ± 0.031	98 ± 1.6
	3.00	3.21 ± 0.051	107 ± 1.6	3.13 ± 0.10	104 ± 3.2

$t_{\text{calc.}} = 0.884$; $t_{\text{tab., } v=8, p=0.05} = 2.31$; $F_{\text{calc.}} = 1.262$; $F_{\text{tab., } v1=8, v2=8, p=0.05} = 3.44$.

therefore, the flow rate of 0.5 mL/min was employed subsequently. The sample volume in the range 60–360 μL was investigated. The absorbance increased with the increase in the sample volume up to 300 μL ; therefore, a sample volume of 300 μL was selected and subsequently used. The effect of reaction coil-I and coil-II lengths in the range 0–300 cm was examined on the diazotization process and formation of azo dye, respectively. The maximum peak height absorbance was obtained when the reaction coil lengths were 200 and 150 cm and further increase in coil lengths had little effect on absorbance. Therefore, the reaction coil-I and coil-II lengths of 200 and 150 cm were chosen and used for further studies, respectively.

The effect of reaction coil temperature in the range 10–50°C was also examined. The maximum absorbance was obtained at 30°C, above which bubbles were observed in the reaction coils probably due to possible dissociation of diazotized sulphanic acid into nitrogen gas. Therefore, the reaction coil temperature of 30°C was fixed and employed for subsequent studies.

3.2. Analytical Figures of Merit. Under the optimum conditions described above, the calibration graph of absorbance versus ANTU concentrations was linear in the range 0.05–120 mg/L. The coefficient of determination (R^2), relative standard deviation ($n = 3$), and regression equation over the range studied were 0.9995 ($n = 7$), 1.8–3.6%, and $y = 0.031x - 0.018$ (where y = absorbance and x = concentration in mg/L), respectively. The limit of detection (LOD) based on the concentration response that equals to three times of the peak-to-peak baseline noise ($S/N = 3$) was 0.01 mg/L. The injection

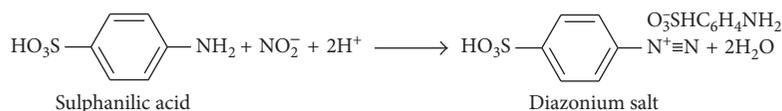


SCHEME 1

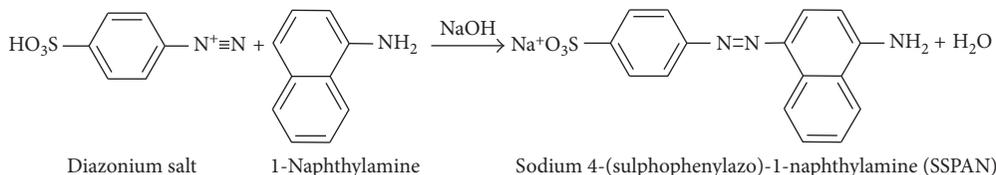
throughput was 45/h. Figure 4 illustrates the chart recorder traces of absorbance at 495 nm for the concentration range of 5–120 mg/L ANTU and a calibration curve in the inset for the same standard solutions.

Table 2 reports the comparison of the analytical characteristics of the proposed method with other methods used for the determination of ANTU. The proposed FI spectrophotometric system has satisfactory linearity, sensitivity, sample throughput, and precision.

3.3. Interferences. The influence of different cations, anions, organic compounds, and some pesticides with and without ANTU was carried out. The tolerable level of these chemical species was selected as the concentration which did not enhance or inhibit the peak height absorbance for ANTU at 0.1 mg/L by more than 5%. No significant effect of Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Mn^{2+} , Fe^{3+} , Co^{2+} , PO_4^{3-} , SO_4^{2-} , Cl^- , and NO_3^- 1000-fold, phenol and humic acid 10-fold, asulam, diazinon, malathion, maneb, nabam, phoxim, terbufos, thiabendazole, and thiram 50-fold was observed. Therefore, the method



SCHEME 2



SCHEME 3

could be easily applied for ANTU analysis in real samples in the presence of the above chemical species.

3.4. Application. The proposed method was successfully applied for the determination of ANTU in natural water samples. Table 3 reports the results of water samples spiked with ANTU standards which were in good agreement with the reported HPLC method [15] with recovery from 93 ± 1.9 to $110 \pm 3.0\%$. There was no significant difference between the variances and mean results of the two methods at 95% confidence level by applying the *F*- and *t*-tests ($t_{\text{calc.}} = 0.884$, $t_{\text{tab.,}\nu=8,p=0.05} = 2.31$, $F_{\text{calc.}} = 1.262$, $F_{\text{tab.,}\nu1=8,\nu2=8,p=0.05} = 3.44$).

3.5. Possible Reaction Scheme. In the alkaline medium, ANTU was hydrolysed and 1-naphthylamine was formed (Scheme 1) [12]. Nitrite was converted into nitrous acid in the acidic medium; subsequent diazotization of sulphanilic acid and formation of diazonium salt are shown in Scheme 2. This salt was then coupled with 1-naphthylamine in an alkaline medium to form sodium 4-(sulphophenylazo)-1-naphthylamine salt (Scheme 3) [9, 23]. The resulting azo dye had shown maximum absorption wavelength at 495 nm.

4. Conclusions

A simple FI spectrophotometric method was developed enabling the quantitation of ANTU with low LOD (0.01 mg/L) and good sample throughput (45/h). Anions and cations and a number of pesticides had no influence on the quantitation of ANTU. The developed procedure was successfully applied for the determination of ANTU in spiked natural water samples using the SPE technique with recovery from 93 ± 1.9 to $110 \pm 3.0\%$. There was no significant difference between the proposed FI spectrophotometric and HPLC method at 95% confidence interval by applying the tests of significance.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgments

This research work was conducted at the Department of Chemistry, University of Balochistan, Quetta, Pakistan.

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