Res Chem Intermed
DOI 10.1007/s11164-012-0888-z

Spectrophotometric analysis of trichloroethylene in various environmental and biological samples

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Received: 9 September 2012 / Accepted: 25 October 2012

Abstract A simple sensitive extractive spectrophotometric method for determination of trichloroethylene is proposed. Trichloroethylene is treated with pyridine to form glutaconic aldehyde by heterolytic cleavage of the pyridine ring. Glutaconic aldehyde is further coupled with 4-aminoacetanilide to form an orange–red dye which is extractable in 3-methyl-1-butanol. The extracted dye shows absorption maximum at 520 nm. The system obeys Beer's law in the range of 0.05–0.8 μg mL^{-1}. Important analytical parameters such as time, temperature, reagent concentration, acidity etc. have been optimized for complete colour reaction. Sandell's sensitivity and molar absorptivity for the system were found to be 0.001 μg cm^{-2} and 1.2×10^5 L mol^{-1} cm^{-1}, respectively. The proposed method is satisfactorily applied to micro-level determination of trichloroethylene in various environmental and biological samples.

Keywords Trichloroethylene · 4-Aminoacetanilide · Pyridine · Spectrophotometry

Introduction

Trichloroethylene (TCE) is one of the most frequently reported organic contaminants in water, being widely distributed in the environment due to industrial discharge of wastewater streams. TCE has been extensively used as a metal degreaser, extraction solvent for adhesives, and dry cleaner, in textile manufacturing, as a chemical intermediate in production of other chemicals, and as a refrigerant. TCE is used in consumer products such as typewriter correction fluids, paint removers/strippers, spot removers and rug-cleaning fluids [1]. It is also used as

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Published online: 20 December 2012

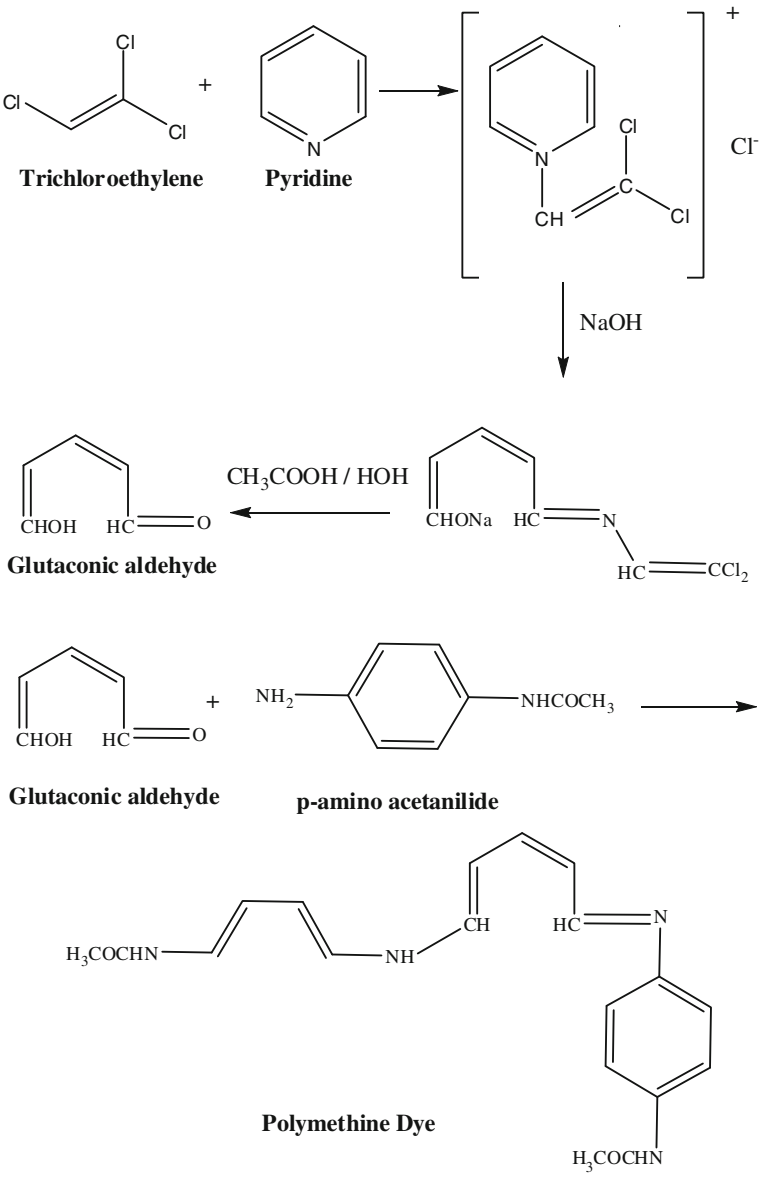
a low-temperature heat-transfer medium, flame-retardant chemical and insecticide. Its historical use in foods, beverages (for detoxification of coffee), pet foods, medicine, pharmaceuticals and cosmetics has been banned because of its toxicity. TCE and other chlorinated aliphatics are present in the majority of contaminated aquifers [2, 3]. TCE is a major groundwater contaminant, and its presence in drinking water is a potential health hazard [4]. Microbial metabolism of TCE under anaerobic conditions can lead to formation of vinyl chloride and dichloroethylene [5], which are also of concern as drinking water contaminants [6]. TCE metabolism is important to overall toxicity, and children may be particularly susceptible to TCE toxicity [7]. Central nervous system effects are the primary effects noted from acute inhalation exposure to TCE in humans, with symptoms including sleepiness, fatigue, headache, confusion and feelings of euphoria. Effects on the liver, kidneys, gastrointestinal system and skin have also been noted [1]. Neurological, lung, kidney and heart effects have been reported in animals acutely exposed to trichloroethylene [1]. A recent analysis of available epidemiological studies reported trichloroethylene exposure to be associated with several types of cancer in humans, especially of the kidney, liver, cervix and lymphatic system [8]. The maximum permissible limit of TCE in drinking water is 0.005 mg L^{-1} as per US Environmental Protection Agency (USEPA) guidelines [9]. The occupational exposure limit time-weighted average (TWA) for an 8-h workday is 50 ppm in air [10]. A value of 25 ppm is proposed as a reference value for work environments [11]. The California Environmental Protection Agency (CalEPA) has calculated a chronic inhalation reference exposure level of 0.6 mg/m^3 based on neurological effects in humans. The CalEPA reference exposure level is a concentration at or below which adverse health effects are not likely to occur [12]. TCE is generally determined by head-space analysis [13], gas chromatography-magnetic sector mass spectrometry [14], headspace gas chromatography [15], quartz crystal microbalance sensor [16], headspace solid-phase microextraction gas chromatography negative chemical ionization mass spectrometry [17], gas chromatography with cryogenic trapping [18] or gas chromatography mass spectrometry [19].

The method proposed herein is a simple spectrophotometric method based on a modified Fujiwara reaction in which TCE is treated with pyridine in alkaline medium to give a coloured Schiff base. The colour of the Schiff base is discharged by adding acetic acid followed by addition of 4-aminoacetanilide. The proposed method has been successfully applied for determination of trichloroethylene in environmental and biological samples (Figs. 1–6; Scheme 1).

Experimental

Apparatus and reagents

A Systronics 166 spectrophotometer was used for spectral measurements. pH measurements were made with a Systronics 335 digital pH meter. All chemicals used were of analytical grade, and double-distilled deionised water was used for preparation of solutions. Solution (1.0 mg mL^{-1}) of trichloroethylene (Aldrich) was prepared in



Scheme 1 Colour reaction of trichloroethylene

alcohol. Working standard was prepared by appropriate dilution of the stock with water. Aqueous solution (2.0 % w/v) of 4-aminoacetanilide (Merck, Mumbai, India) was prepared. NaOH (5.0 M) aqueous solution was prepared in deionised water. Glacial acetic acid (Aldrich) and pyridine (Merck, Mumbai, India) were used.

Procedure

To construct a calibration curve, 50-mL sample solutions containing trichloroethylene in the range of 0.05–0.8 μg were taken in a conical flask, and 1 mL pyridine was added, followed by addition of 2 mL 5 M NaOH and thorough shaking. The contents were kept in a water bath at 70 °C for 3 min and shaken from time to time. A pinkish-red ring was obtained, which was cooled in ice-cold water, then the colour of the ring was discharged by adding 1 mL glacial acetic acid dropwise. To this solution, 1 mL 2 % 4-aminoacetanilide solution was added, and the content was allowed to stand for 10 min. The orange–yellow product obtained was extracted in 2.5× 2 mL 3-methyl-1-butanol. The extract was dried over anhydrous sodium sulphate, and the absorbance was measured at 520 nm against 3-methyl-1-butanol.

Results and discussion

Spectral characteristics and method validation

The absorption spectra of the final coloured product showed maximum absorbance at 520 nm. The reagent blank had negligible absorbance at this wavelength. Beer's law was obeyed over the concentration range of 0.05–0.8 μg mL^{-1} in extracted medium. The molar absorptivity and Sandell's sensitivity were found to be 1.2×10^5 L mol^{-1} cm^{-1} and 0.001 μg cm^{-2}, respectively. The slope, intercept and correlation coefficient were evaluated by least-squares regression analysis and are also presented in Table 1.

Precision of the method was checked by seven replicate analyses of solution containing 15 μg trichloroethylene in 50 mL final solution. The standard deviation and relative standard deviation were found to be 0.002 and 0.310 %, respectively (Table 1).

Table 1 Spectral characteristics, precision and accuracy of the proposed method

Parameter	Result
λ_{max} (nm)	520
Range of Beer's law (μg mL^{-1})	0.05–0.8
Stability of colour	~24 h
Molar absorptivity (L mol^{-1} cm^{-1})	1.2×10^5
Sandell's sensitivity (μg cm^{-2})	0.001
SD	0.002
Relative SD (%)	0.310
Regression equation	$(Y = bX + a)$
Correlation coefficient	0.999
Slope (b)	1.9
Intercept (a)	0.001

X concentration in μg mL^{-1}

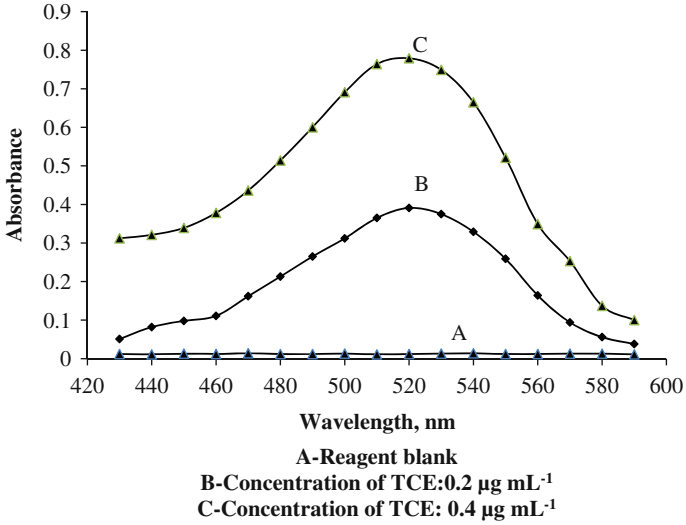


Fig. 1 Absorption spectra of the coloured product and reagent blank

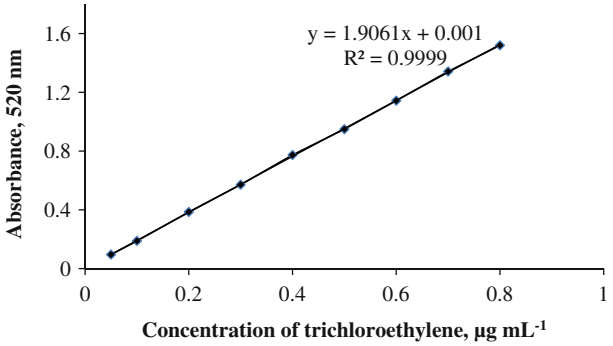


Fig. 2 Calibration curve for trichloroethylene determination

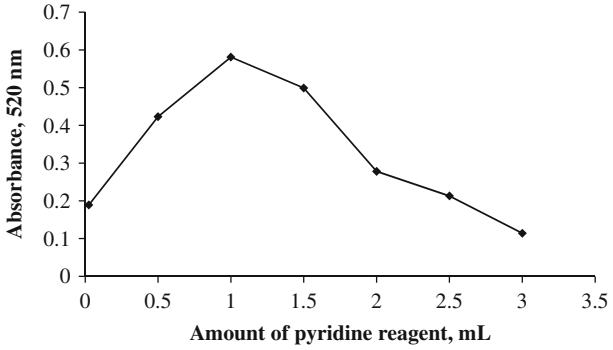


Fig. 3 Effect of amount of pyridine reagent

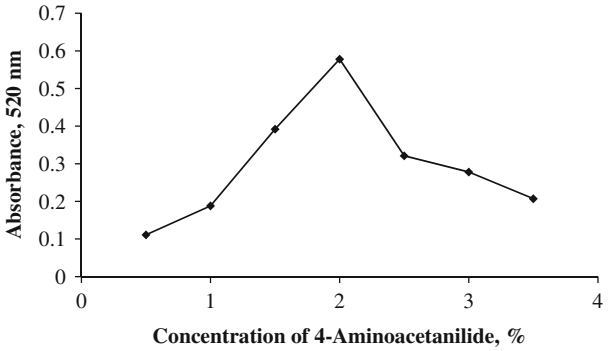


Fig. 4 Effect of concentration of 4-aminoacetanilide

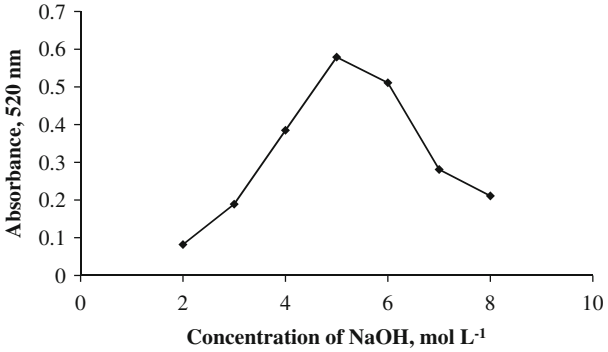


Fig. 5 Effect of concentration of NaOH

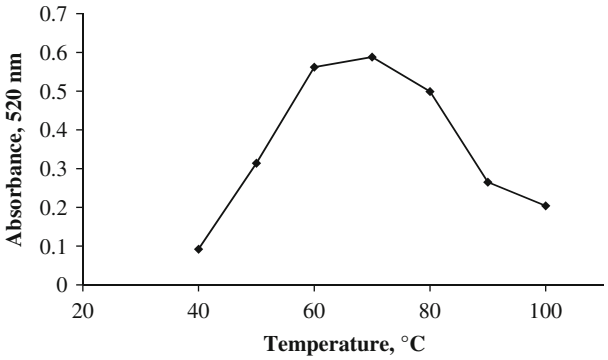


Fig. 6 Effect of temperature on sensitivity

Effect of reagent concentration

Under the proposed reaction conditions it was found that 1 mL pyridine and 2 mL 1 % 4-aminoacetanilide were required for complete colour development.

Table 2 Effect of diverse ions (concentration of TCE: 15 μg in 50 mL)

Foreign species	Tolerance level* (μg mL^{-1})	Foreign species	Tolerance level* (μg mL^{-1})
DDT	1,000	CH_3CHO, $C_6H_5NO_2$	500
Carbaryl, Propoxur	500	$C_2H_5OC_2H_5$	450
2,4-D,2,4,5-T	300	Cd^{2+}, Cu^{2+}	600
Paraquot	150	NO_2^-, Sn^{2+}	400
Malathion, CCl_4		Ca^{2+}, Ni^{2+}	
Parathion	100	Hg^{2+}	300
C_6H_6, C_2H_5OH	650	PO_4^{3-}	100

* Causing ±2 % variation in absorbance value

Effect of temperature, time and pH

Under the optimum condition, the final absorbance was measured at pH 5.0–5.5. No adverse effects on colour development were found for temperature in the range of 25–35 °C, and 10 min was sufficient for complete colour development after addition of the reagent.

Effect of foreign species

The effect of diverse ions expected to coexist with TCE was studied by adding a known amount of different organic pollutants and inorganic ions to a test solution containing 15 μg TCE per 50 mL final volume. The method was found to be free from most interferences. Trichloroacetic acid and chloroform gave positive interference since they also give Fujiwara reaction. The tolerance limits shown in Table 2 are the concentration of interfering species that cause ±2 % variation in absorbance value.

Colour reaction

The reaction involves three steps:

1. TCE is treated with pyridine in alkaline medium to form a pink-coloured ring of Schiff base of glutaconic aldehyde;
2. The Schiff base is converted to glutaconic aldehyde by adding acetic acid;
3. Glutaconic aldehyde forms an orange–red-coloured polymethine dye with 4-aminoacetanilide.

Applications

Determination of TCE in environmental samples

Water samples (5 mL) were taken and fortified with known amount of TCE, then analysed by the proposed method (Table 3).

Table 3 Determination of TCE in environmental samples

S. no.	Samples	Amount of TCE added (μg)	Amount of TCE found* (μg)	Recovery (%)	RSD (%)
1	Tap water (5 mL)				
	(S_1)				
	A	10	9.82	98.20	1.20
	B	20	19.81	99.05	1.01
	C	30	29.50	98.33	0.96
	(S_2)				
	A	10	9.87	98.7	0.98
	B	20	19.85	99.25	0.99
	C	30	29.82	99.4	1.02

A, B, and C are three different samples

* Mean of analysis of three replicates

Table 4 Determination of TCE in biological samples

S. no.	Samples	Amount of TCE added (μg)	Amount of TCE found* (μg)	Recovery (%)	RSD (%)
1	Urine (5 mL)				
	(S_1)				
	A	10	9.86	98.6	1.01
	B	20	19.73	98.65	1.02
	C	30	29.52	98.4	0.96
	(S_2)				
	A	10	9.82	98.2	1.12
2	B	20	19.53	97.65	1.20
	C	30	29.66	98.86	1.18
	Blood serum (2 mL)				
	(S_1)				
	A	10	9.85	98.5	1.16
	B	20	19.83	99.15	1.12
	C	30	29.50	98.33	1.21
	(S_2)				
	A	10	9.79	97.9	1.18
	B	20	19.56	97.8	1.15
	C	30	29.67	98.9	1.11

A, B, and C are three different samples

* Mean of analysis of three replicates

Determination of TCE in biological samples

A known amount of trichloroethylene was added to free urine and blood serum samples. After deproteinization, the samples were allowed to stand for 2 h and

centrifuged, then analysed by the proposed method. Recovery was found to be ~98 and ~97 %, respectively (Table 4).

Conclusions

The proposed method is simple, sensitive and rapid compared with other methods for TCE determination. The rapid colour development, reproducibility, stability and easy availability of the reagent and freedom from a large group of interfering species are some advantages of the method. Extraction method lowers the detection limit.

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