

A sensitive spectrophotometric method for determination of carbon tetrachloride

Sukumar Chatterjee* and V. K. Gupta

Department of Chemistry, Govt. V.Y.T. P.G. Autonomous College, Durg-491 001, India

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A sensitive spectrophotometric method for the determination of carbon tetrachloride (CTC) in ppm level is described. The method involves the modification of the Fujiwara reaction i.e. discharging the colour with glacial acetic acid followed by addition of *p*-aminoacetophenone reagent which results in the formation of the purple red coloured polymethine dye having an absorption maximum at 495 nm. Beer's law is obeyed in the range of 4.0–36 μg (0.4–3.6 ppm) of carbon tetrachloride per 10 ml of solution. The sensitivity of the conventional Fujiwara procedure is increased after this modification. The method has been successfully applied for the determination of carbon tetrachloride in air, laundry air and biological samples.

Carbon tetrachloride is generally determined by chromatography, such as gas chromatography¹, gas liquid chromatography², coulometry³ and spectrophotometrically using Fujiwara reaction^{4,5}, in which polychlorinated compounds like chloroform, trichloroacetic acid and trichloroethylene reacts with pyridine and alkali which form red colour dye on heating. Most of the earlier reported methods^{6,7} used benzidine as a reagent, which is reported to be carcinogenic⁸, while the method using sulphanilic-formic acid reagent⁹, is less sensitive than the proposed method.

A sensitive method based on modified Fujiwara reaction using *p*-aminoacetophenone has been developed for the determination of carbon tetrachloride and related compounds. The red colour obtained by Fujiwara reaction is discharged with glacial acetic acid and solution is treated with *p*-aminoacetophenone in acidic medium to give a purple red colour dye which has an absorption maximum at 495 nm. The reaction was earlier used for the determination of chloroform¹⁰ and trichloroacetic acid^{11,12}. The method has been successfully applied for the determination of carbon tetrachloride in air, laundry air and biological samples.

Results and discussion

Effect of reagent concentration : 1 ml pyridine reagent and 1 ml of 5 M sodium hydroxide were required for maximum colour intensity. Excess of pyridine reagent reduced the colour intensity of the final solution. Higher amount of sodium hydroxide made the solution slightly turbid where as lower amounts did not produce the same intensity of colour. Drop wise addition of glacial acetic acid is necessary for decolourisation of the red colour. A minimum of 1 ml of PAAP was required for maximum colour intensity. Excess amount of PAAP decrease the intensity of the colour.

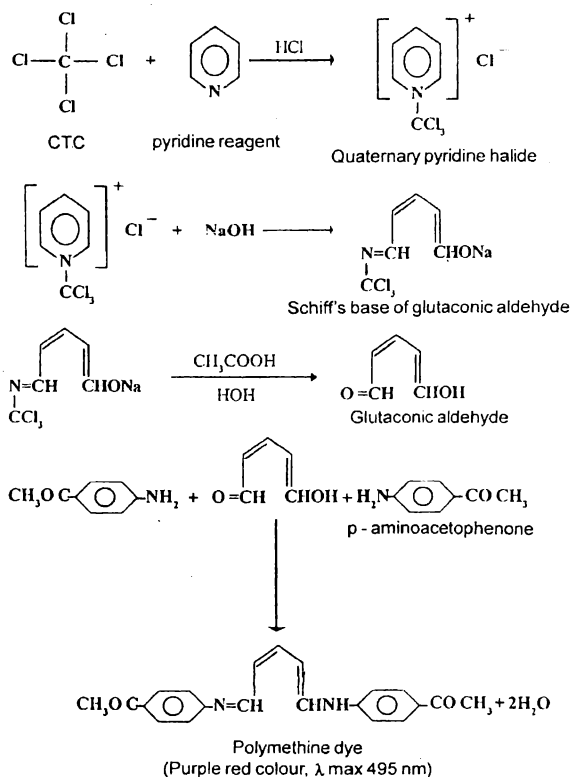
Beer's law is obeyed in the range of 4–36 μg of CTC per 10 ml (0.4–3.6 ppm) of solution. Molar absorptivity and Sandell's sensitivity was found to be $3.58 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and 0.0044 $\mu\text{g cm}^{-2}$ respectively. The reproducibility of the method was checked by such replicate analyses of a solution containing 20 μg of CTC in 10 ml (Fig 1). The standard deviation and relative standard deviation were found to be ± 0.0081 and 1.76% respectively.

Effect of temperature, time and pH : It was observed that heating of the reaction mixture for a ~5 min in a water bath at 70°C gave optimal absorbance values. After heating for more than 5 min absorbance value decreases. Maximum absorbance values were observed between pH 1–2. The purple red coloured dye was found to be stable for ~15 min and after 15 min showed gradual decrease in the intensity.

Effect of diverse ions : Effect of various diverse ions and polyhalogenated compounds on the reaction was studied by adding known amount of these compounds to a solution containing 20 μg of carbon tetrachloride per 10 ml (2 ppm). The tolerance limit for the compound studied are given in Table 1. The method was found to be free from interference of various organic solvents like benzene, ether, alcohol and aldehyde. Chloroform gave positive interference.

Colour reaction : The colour reaction takes place in three steps.

In the first step, carbon tetrachloride reacts with pyridine reagent in alkaline medium to form Schiff's base of glutaconic aldehyde. In the second steps by the addition of glacial acetic acid, the red colour of Schiff's base of glutaconic aldehyde is converted to yellow coloured glutaconic aldehyde. In the third step, which form a purple red coloured polymethine dye with *p*-aminoacetophenone reagent (Scheme 1).



Scheme 1. Colour reaction of carbon tetrachloride.

Table 1. Effect of foreign species

Concentration of CTC in 20 mg/10 ml = 2 ppm

Foreign species	Tolerance limit (ppm)
Acetone	2450
Dimethylformamide (DMF)	1750
Iso-amylalcohol	1500
DDT	1250
Benzene, methanol	1050
Carbaryl, propoxar	600
2,4-D, 2,4,5-T	450
Paraquat, BHC	300
Malathion	250
Parathion	150
Fe^{3+}	1200
Cu^{2+} , Cd^{2+} , Fe^{2+}	1050
Cl^- , SO_4^{2-}	950
Pb^+ , K^+ , Na^+	550
Sn^{2+} , Ca^{2+} , Ni^{2+}	450
NO_2^-	350
Hg^{2+}	250
PO_4^{3-}	150

*Tolerance limit is the amount of interference that causes an error $\pm 2\%$.

Experimental

A Systronics 106 digital spectrophotometer is used for all spectral measurement, a Systronics 335 pH meter is used for pH measurement. The air was sampled with midget impingers of 35 ml capacity and flow rate was controlled by rotameter.

All the reagents used were A.R. grade and double distilled water was used throughout the study. Carbon tetrachloride (E. Merck) pure distilled carbon tetrachloride (1 mg/ml) was prepared in 20% alcohol. Working standard was prepared by appropriate dilution of stock solution. *p*-Aminoacetophenone (PAAP, Ferak, Berlin)-1% solution of A.R. grade PAAP in 25% alcohol. Sodium hydroxide-5.0 *M* aqueous solution was used. Hydrochloric acid-10 *M* aqueous solution was used. Pyridine reagent is prepared by adding 3 ml of concentrated hydrochloric acid to 18 ml of pyridine and then 12 ml of distilled water. Glacial acetic acid-A.R. grade was used.

Procedure : Aliquots containing 4–36 μg (0.4–3.6 ppm) of carbon tetrachloride was taken in a 10 ml calibrated test tube. 1 ml of pyridine reagent and 1 ml of 5.0 *M* sodium hydroxide were added to it and thoroughly shaken. The contents were kept in water bath at 70°C for ~5 min and shaken from time to time. The red coloured solution so obtained was cooled in ice cold water and then decolourised with drop wise addition of glacial acetic acid. 1 ml of PAAP solution and 2 ml of 10 *M* hydrochloric acid were added and the contents were allowed to stand for 10 min. The volume was made up to 10 ml and the absorbance of purple red colour dye was measured at 495 nm against a reagent blank, which was colourless.

Application :

In air : Known amount of carbon tetrachloride was evaporated by gentle heating in an impinger and was absorbed in to another impinger containing 5 ml pyridine reagent and connected serially to a source of suction. The air was sampled for ~30 min at the rate of 0.5 L min^{-1} . The amount of carbon tetrachloride in the absorbing solution was determined by the recommended procedure. The recoveries varied for 96–98% (Table 2).

Laundry air : Carbon tetrachloride is an important ingredient for the dry cleaning solvent in laundry works. Hence it was analysed in laundry air. During the use of solvent it comes in the laundry air^{2,3}. Three impingers containing 5 ml of pyridine reagent was connected to a source of suction and laundry air was sampled for ~30 min at the rate of 0.5 L min^{-1} at the rate of 0.5 L min^{-1} . The samples

Table 2. Determination of CTC in air and biological samples

Samples	CTC originally found (μg)	CTC added (μg)	CTC found (μg)		% of recovery	
			Present method	Reported method ⁸	Present method	Reporte method ⁸
Air (15 L)	–	12	11.55	11.18	96.3	93.2
	–	16	15.53	15.13	97.1	94.6
	–	20	19.68	19.02	98.4	95.1
Laundry air (15 L)	6.45	10	15.97	15.56	97.1	94.6
	7.39	10	16.97	16.53	97.6	95.1
	8.17	10	17.86	17.37	98.3	95.6
Blood (2 ml)	–	12	11.41	11.07	95.1	92.3
	–	16	15.40	14.84	96.3	92.8
	–	20	19.42	18.64	97.1	93.2
Urine (2 ml)	–	16	15.24	14.68	95.3	91.8
	–	20	19.38	18.48	96.9	92.4
	–	24	23.42	22.34	97.6	93.1

were then analysed by the proposed and reported method⁸ (Table 2).

In biological samples : 2 ml of carbon tetrachloride free sample of blood and urine was taken and known amount of carbon tetrachloride was added before deproteination and the mixture was allowed to stand for 2 h and then analysed by the proposed and reported method⁸. The recovery was found to be ~97% (Table 2).

Conclusion : The present method is found to be more sensitive as compared to the conventional Fujiwara reaction and other reported spectrophotometric methods. The method is also free from the interference of many organic solvents as well as cations and anions.

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