Indian Journal of Chemical Technology
Vol. 15, May 2008, pp. 306-309

A simple and sensitive method for determination of carbon disulphide in environmental and biological samples

Urmila Tamrakar[a], V K Gupta[b], Sunitha B Mathew[a] & Ajai K Pillai [a*]

[a]Chemistry Department, Govt. V.Y.T. PG Autonomous College, Durg 491 001, India

[b]School of Studies in Chemistry, Pt. Ravishankar Shukla University, Raipur 492 011, India

Email: drajaipillai@gmail.com

Received 1 February 2007; revised 3 March 2008

An analytical method using potassium dichromate and diphenylcarbazide for determination of carbon disulphide has been proposed. In this method carbon disulphide reduces the Cr(VI) to Cr(III) and the unreduced Cr(VI) forms a pink-purple complex with diphenylcarbazide in acidic medium, which is measured spectrophotometrically at 530 nm. Beer's law is obeyed over a concentration range of 0.01 to 0.1 μg mL^{-1}. Molar absorptivity and Sandell's sensitivity were found to be 5.5×10^5 L mol^{-1} cm^{-1} and 0.00013 μg cm^{-2} respectively. The optimum reaction conditions and other analytical parameters were evaluated. The effect of interfering ions on the determination of CS_2 was studied. The method has been successfully applied for the determination of CS_2 in grain samples, fungicides (ziram, thiram) and various environmental and biological samples.

Keywords: Spectrophotometric method, Carbon disulphide, Diphenylcarbazide, Potassium dichromate

Carbon disulphide is used in industry in the production of viscose rayon fibers[1]. It is also used, to some extent, as a solvent in various industrial processes including the refining of paraffin and petroleum, and more recently in the production of flotation agents and herbicides[2]. Carbon disulphide was one of the first fumigants employed on a large scale. Its use, against the grape phylloxera is a landmark in the history of applied entomology. For many years CS_2 was widely used as a soil or space fumigant. Its tendency to burn or explode presents a hazard, and many explosions have been recorded during its use as a fumigant[3]. The threshold limit[4] value of carbon disulphide in air is 10 μg mL^{-1}.

Carbon disulphide is toxic to humans. High concentrations of the vapour produce narcotic effect and on continuous exposure, unconsciousness and death may result due to paralysis of the respiratory centers. Repeated exposure to even low concentrations for periods of few weeks or longer may result in a variety of nervous manifestations[5,6]. Acute and sub acute poisoning occurs with short exposure to carbon disulphide concentrations ranging between 3000-5000 mg m^{-3} with predominantly psychiatric and neurological signs and symptoms such as extreme irritability, uncontrolled anger, rapid mood changes including maniac, delirium and hallucinations, suicidal tendencies. Other symptoms include memory defects, severe insomnia, nightmares, fatigue, loss of appetite, gastrointestinal troubles and asthenia[7].

Various instrumental methods such as gas chromatography[8,9], gas liquid chromatography[10], photo ionization detector[11] and spectrophotometric methods[12,14] are reported for the determination of carbon disulphide.

In the present work, a simple sensitive spectrophotometric method using potassium dichromate and diphenylcarbazide for the determination of carbon disulphide and dithiocarbamate fungicides in various environmental, biological and grain samples is reported. The reaction is based on the reduction of chromium (VI) with CS_2 to chromium (III), the unreduced chromium (VI) forms pink purple complex with diphenylcarbazide in acidic medium. The absorbance of the resulting complex was measured at 530 nm.

Experimental Procedure

Apparatus

A Toshniwal TVSP (model-25) visible spectrophotometer and a Systronic digital pH meter (model-335) were used for spectral and *p*H measurements, respectively. Fritted midget impingers (diameter 10 mm) of 35 mL capacity were used for air sampling; flow rate was adjusted by calibrated rotameter used for air flow measuring.

Reagents

All the reagents used were of analytical reagent grade. Double distilled water was used throughout the experiment. Stock solution of carbon disulphide

(Qualigens fine chemical, Mumbai): 1 mg mL^{-1} solution of carbon disulphide was prepared by dissolving 100 mg carbon disulphide in 100 mL of 50% ethanol[15]. Working standard was prepared by appropriate dilution of the stock. 0.1% solution of diphenylcarbazide (Loba chemie, Mumbai) was prepared in 25% acetone; 0.01% (*w*/*v*) solution of potassium dichromate (Oster, Calcutta) was prepared in distilled water. The 5% ethanol (Merck, Mumbai) solution was used as absorbing solution. Stock solution of dithiocarbamate fungicides (Ziram and Thiram): 1 mg mL^{-1}solution of ziram (80%, BASF India Ltd, Thane) and thiram (75%, Devidayal Agrochemical Ltd, Mumbai) was prepared in 0.1 mol L^{-1} EDTA and 0.1 mol L^{-1} sodium hydroxide respectively.

Method

An aliquot containing 0.01 to 0.1 μg mL^{-1} of CS_2 was taken in a 25 mL standard flask and to it 0.5 mL of potassium dichromate was added. The content of the flask was left for 5 min for reduction of Cr(VI) to Cr(III). To this, 0.25 mL of concentrated sulphuric acid and 7.5 mL of diphenylcarbazide were added, the unreduced Cr(VI) forms pink purple complex with diphenylcarbazide[15]. The complex was made up to the mark with distilled water and its absorbance was measured at 530 nm against reagent blank, which gave maximum absorbance at this wavelength. The decrease in absorbance corresponding to the unreduced Cr(VI), which reflects the carbon disulphide concentration was obtained by subtracting the decrease in absorbance of the test solution (complex minus test) from that of the blank solution (complex minus blank). Calibration graph was prepared by plotting the decrease in absorbance of complex against the amount of carbon disulphide.

Collection and analysis of air samples

As the laboratory air did not contain carbon disulphide, contaminated air sample was prepared by spraying and warming carbon disulphide in a fuming cupboard. Three midget impingers each containing 5 mL of ethanol as an absorbing solution was connected in series to an air sampling train[16] attached to the suction pump placed outside the chamber. The air from the fume cupboard was then passed through the impingers at a flow rate of 0.75 L min^{-1}. Aliquots of the solution was taken and analyzed by the proposed method.

Results and Discussion

The maximum absorbance of pink-purple complex was obtained at 530 nm (Fig. 1). The reaction scheme is given in Fig. 2.

Adherence to Beer's law, molar absorptivity, Sandell's sensitivity

The response was linear between concentration range 0.01 to 0.1 μg mL^{-1} of carbon disulphide. Molar absorptivity and Sandell's sensitivity were found to be 5.5×10^{5} L mol^{-1} cm^{-1} and 0.00013 μg cm^{-2} respectively.

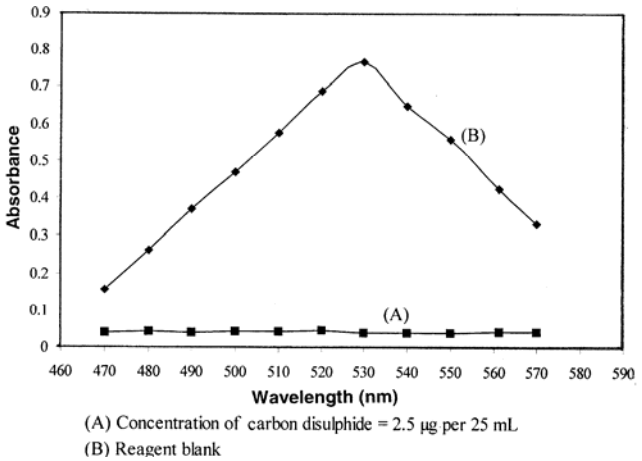
Reproducibility

Reproducibility of the method was checked by six replicate analyses of a solution containing 2 μg per 25 mL of CS_2 by six replicate analyses. The standard deviation and relative standard deviation of absorbance values were found to be ±0.008 and 2.8% respectively. The correlation coefficient value of the curve was found to be 0.98. The detection limit was found to be 0.024 μg mL^{-1}.

Effect of various analytical parameters

Collection efficiency

It was found that absorption of CS_2 was complete in the first impinger; where as the second and third impingers showed negligible decrease in absorbance. 5 mL of 5% ethanol was sufficient for absorption of CS_2 at a flow rate of 0.75 L min^{-1}.



(A) Concentration of carbon disulphide = 2.5 μg per 25 mL
(B) Reagent blank

Fig. 1—Absorption spectra of chromium complex and reagent blank

$$CS_2 + Cr^{6+} \rightarrow Cr^{3+}$$

$$\underset{\text{Unconsumed}}{Cr^{6+}} + \text{Diphenyl carbazide} \xrightarrow[\text{Acid}]{\text{Conc. } H_2SO_4} \underset{\lambda \text{ max } 530\text{ nm}}{\text{Pink purple complex}}$$

Fig. 2—Reaction scheme

Effect of pH

The effect of acidity on the colour reaction was studied and it was found that the pink-purple complex was formed under highly acidic condition. It was found that 0.25 mL of concentrated sulphuric acid was necessary for complete color development.

Effect of reagent concentration

In the colour reaction, the effect of various reagents was studied and found that 0.5 mL of 0.01% Cr(VI), 7.5 mL of 0.1% diphenylcarbazide reagent and 0.25 mL of concentrated sulphuric acid was sufficient for maximum colour development in blank.

Effect of foreign species

The effect of common foreign species and pesticides, which are likely to interfere in the determination of CS_2 was studied. Known amount of foreign species and pesticides were added to a standard solution containing 2 μg of CS_2 in 25 mL of final solution (Table 1). Hydrogen sulphide was found to interfere, which can be eliminated by absorption in lead acetate prior to the passing of CS_2

Application of method

Determination of carbon disulphide in biological samples

The samples were prepared by adding known amount of carbon disulphide in blood and urine samples. The samples were deproteinsed with trichloroacetic acid and extracted with 2 × 5 mL of ethanol. The residue was dissolved in ethanol[14]. Aliquots were taken in 5 mL standard flask and analyzed as described in the procedure (Table 2).

Determination of carbon disulphide releasing fungicides

Dithiocarbamate fungicides release CS_2 on acid hydrolysis[17]. Addition of hot 9 mol L^{-1} sulphuric acid to fungicides release CS_2, which was absorbed in 5 mL 5% absorbing solution at rate 0.75 L min^{-1}. Aspiration was carried out for 30-40 min[13]. After sampling, the absorbing solution was transferred to 25 mL graduated tube and analyzed by proposed method.

Determination of fungicides in vegetable samples

Different samples of vegetables free from dithiocarbamate fungicides were taken. The samples were spiked with known amount of pesticides and kept overnight. Weighed samples were washed with 50 mL of water, from which fungicide was extracted by 2 × 5 mL of ethanol. The extract was evaporated to dryness and residue (ziram and thiram) dissolved in

Table 1—Effect of foreign species and pesticides (concentration of of carbon disulphide = 2 μg per 25 mL

Foreign species and pesticides	Tolerance limit* (μg mL^{-1})
Ca^{2+}, Ba^{2+}, Sr^{2+}	6,000
Fe^{3+}, Cd^{2+}	1,250
Al^{3+}, Bi^{3+}, Ce^{3+}	1,000
Cu^{2+} , Co^{2+}	450
Sn^{4+}	250
Mn^{4+}, Hg^{2+}	25
NO^{3-}	1500
Mencozeb, ferbam	50

*The amount causing an error of ± 2 % in absorbance value

Table 2—Determination of carbon disulphide in biological samples

Samples	Amount of CS_2		Recovery %	
	Added* (μg)	Found* (μg)	(A)	(B)
Blood*	1	0.97	97.00	96.00
	2	1.95	97.5	93.00
Urine*	1	0.95	95.00	96.00
	2	1.96	98.00	97.60

*Mean of six replicate analyses.
(a) Amount of samples (2 mL)
(A) Proposed method and (B) Reported method[14]

Table 3—Determination of carbon disulphide in spiked environmental samples

Samples	Amount of fungicide		Recovery %	
	Added* (μg)	Found* (μg)	(A)	(B)
In air[a]	5	4.87	97.40	96.60
(10 L)	10	9.79	97.90	98.00
Polluted	5	4.90	98.00	97.00
water[b]	10	9.85	98.50	98.00
(50 mL)	15	14081	98.70	98.00
Grain[b]	5	4.87	97.40	97.20
Samples[b]	10	9.85	98.50	97.00
(10 g)	15	14.75	98.33	97.99
Cabbage[b]	5	4.85	97.00	96.00
(10 g)	10	5.09	90.91	81.62
Lettuce[c]	10	9.71	96.13	97.00
(10 g)	20	19.63	98.50	97.66
Tomato[c]	10	9.65	96.50	96.00
(10 g)	20	19.55	98.55	96.55

*Mean of six replicate analyses
(a) Air was analyzed
(b) Samples spiked with ziram and
(c) Samples spiked with thiram
(A) Proposed method and (B) Reported method[14].

5 mL of 0.1 mol L^{-1} EDTA and 0.1 mol L^{-1} sodium hydroxide respectively and analyzed by the proposed and reported method [14] (Table 3).

Determination of ziram in grain samples

Ziram free grain (wheat) samples were taken in a standard flask, and fortified with known amount of fungicide and extracted with 5 mL of ethanol. The samples were subsequently analyzed by the method described above and compared with reported method[14] (Table 3).

Determination of carbon disulphide (ziram, thiram) in polluted water

Run off water samples were collected from agricultural field where ziram, thiram were used as fungicides. Water samples were filtered and washed with 0.1 mol L^{-1} EDTA. Aliquots were taken in an impinger and analyzed as described in the determination of CS_2 releasing fungicides by proposed method[17] (Table 3).

Conclusion

The proposed method provides a sensitive method for determination of CS_2. The method was found to be free from the interference of a large number of foreign species and toxic reagents. The method can be applied for determination of CS_2 releasing pesticides in grain, environmental and biological samples.

Acknowledgement

The authors are grateful to Chemistry Department of Government V.Y.T. PG. Autonomous, College, Durg (Chhattisgarh)-India for providing laboratory facilities.

Reference

1 Brieger H & Teisinger L, *Toxicology of Carbon Disulphide* (Excerpta Medica Foundation, Amsterdam), 1967, 32.
2 Jacobs M B, *The Analytical Toxicology of Industrial Inorganic Poisons* (Interscience Publishers, New York), 1967, 552.
3 Furton, Kenneth G, Bruna , Juan, Almirall & Jose R, *J High Resolut Chromatoger*, 124 (1996) 369.
4 ACGIH–American Conference of Governmental Industrial Hygienists, *Documentation of the threshold limit values for chemical substances in the workroom environment*, 1986. .
5 Ellenhorn M J & Barceloux D G, *Medical Toxicology, Diagnosis and Treatment of Human Poisoning* (Elsevier, Amsterdam), 1988.
6 Ruijten M W, Salle H J A, Verberk M M & Muijser H, *Br J Ind Med,* 47 (1990) 589.
7 Vigliani E C, *Chronic Carbon Disulfide Poisoning. A report on 100 cases, Med. Lavoro,* in Italian, 1946, 37: 165.
8 Peltonen K J, *Chromatoger*, 464 (1989) 422.
9 Simo R & Grimalt-Joan O, *J Chromatoger A,* 726 (1996) 161.
10 Toyoda M, Suzuki H, Ito Y & Iwaida M, *J Food Sci,* 43 (1987) 1287.
11 Smith D B & Krause L A, *Am Ind Hyg Assoc J,* 39 (1978) 939.
12 Lambert D L, Hatch G L & Moiser B, *Anal Chem,* 47 (1975) 915.
13 Malik A K & Fabula W, *Talanta,* 52 (2000) 341.
14 Agrawal V, Shivhare P & Gupta V K, *Fres J Anal Chem*, 344 (1992) 350.
15 Bassett J E, Denney R C, Jeffery G H & Mendham J, *Vogel's Text Book of Quantitative Inorganic Analysis,* 4th edn (ELBS, London), 1986.
16 Kaveeshwar R & Gupta V K, *Atmospheric Environ*, 26 (1992) 1025.
17 Kesari R & Gupta V K, *Talanta*, 45 (1998) 1097.